

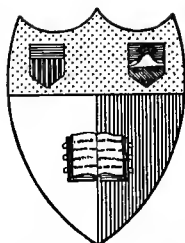
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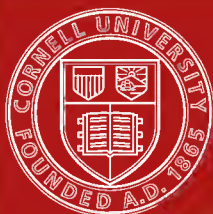
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The "Gas World" Series

# **BENZOL**

**ITS RECOVERY, RECTIFICATION AND USES**



# BENZOL

## ITS RECOVERY, RECTIFICATION AND USES

BY

**S. E. WHITEHEAD**

**B.Sc. Eng., Lond., F.C.S.**

MEMBER OF THE INSTITUTION OF GAS ENGINEERS

WITH AN INTRODUCTORY NOTE BY THE

**Rt. Hon. LORD MOULTON**

**P.C., G.B.E., K.C.B., F.R.S.**

LATE DIRECTOR-GENERAL OF EXPLOSIVES SUPPLY,  
PAST PRESIDENT OF THE INSTITUTION OF GAS ENGINEERS

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## PREFACE

THIS volume is intended as a guide in the principles and practice of benzol recovery, chiefly applied to gasworks. Whilst I have aimed at making the book as practical as possible, and as short as is consistent with clearness, I have endeavoured to explain also the theory upon which the various operations are based; since for the success of any technical process a careful regard for the underlying scientific principles is essential. During the war the Gas Industry made a splendid response to the country's call for benzol and toluol, and those who have the best interests of that industry and of the nation at heart are anxious to see the process of benzol recovery greatly extended throughout the country, as soon as conditions with regard to supplies will permit. Recent legislation tends towards greater freedom in this and in other directions.

Benzol is a valuable commodity, and it is quite certain that its recovery can be made commercially profitable on almost every gasworks. The use of the product as a motor fuel—for which purpose the great bulk will eventually be marketed—has the two-fold advantage of reducing imports and of increasing the revenue of the gas industry, thereby tending to reduce the price of gas and assisting in the conservation of our national resources.

It is confidently expected that many more benzol recovery plants will ultimately be brought into operation, and I trust that the present work will be of some help—as a substitute in some degree for the advice given by the technical staff of the Department of Explosives Supply during the war.

Sections on the rectification of benzol and the utilisation of its products have been added in order to render the book more complete. It will be appreciated, however, that as regards such wide subjects as the manufacture of dyes and explosives, the available space will permit of only a summary of the many ramifications.

Lord Moulton has honoured me by writing an Introductory note, and for that I am greatly indebted. My thanks are also due to several friends, particularly Messrs. T. F. E. Rhead, M.Sc.,

and J. E. Grainger, F.C.S., for valuable assistance in certain sections; and to the following firms who have kindly placed drawings and information at my disposal:—Messrs. The Chemical Engineering Co.; W. C. Holmes, Ltd.; R. & J. Dempster, Ltd.; and Simon Carves, Ltd.

S. E. WHITEHEAD.

PORTSMOUTH, *August*, 1920.

## INTRODUCTORY NOTE

DURING the late War the production and treatment of benzol were matters in the first rank of importance in the departments occupied with providing high explosives for the Allies. In France they took first place, and although in Great Britain the importance of benzol was overshadowed by that of toluol, yet it ranked very high on its own merits; and the fact that France depended largely, if not mainly, on Great Britain for its supplies of crude benzol made the collection of benzol from all possible sources open to us an imperative need of the Allies throughout the whole War.

The normal pre-war production would have been far from adequate to the requirements, and, therefore, the practice of extracting benzol from coal-gas (whether provided by gas companies or at coke ovens), either by oil or tar washing, was instituted and became well-nigh universal, and it is to it that we must attribute the sufficiency of our supplies. The author of this book, Mr. S. E. Whitehead, was a most efficient member of my staff at the Explosives Supplies Department, and was especially concerned with this part of its work, and I am greatly pleased to find that he is seeking to give the world in a permanent form the results of his practical knowledge of the subject as perfected by the experience gained in the service of the Department, so that the knowledge so gained may not be lost. He is eminently fitted to perform this task, and I wish all success to his endeavours.

War is a long and disheartening tale of the destruction of that which the human race has accumulated by its industry and labour. There is little to save from the wreck in comparison with the vast bulk of that which is a total loss. But, like all other concentrations of human effort, it brings with it some return in the way of new experience and wider knowledge, and it is our duty to take care that this gain is not allowed to escape us. I trust that this book will perpetuate what we

have thus learned about the production, rectification, and use of benzol, the compound which, above all others, constitutes the foundation of industrial organic chemistry. At present it is humiliating to think that its most profitable economic use is to be burnt. How long will this be the best that we can do with it ?

MOULTON.



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# PART I

## THE RECOVERY OF BENZOL FROM GAS

### CHAPTER I INTRODUCTORY

BENZOL or benzole is the name usually applied in the chemical industry to a mixture of hydrocarbons of the benzene series, in which benzene itself predominates, in association with certain of its homologues and various impurities. The term is not applied to any particular mixture or quality of liquids, but is usually prefixed by a reference to the strength or degree of purity, *e.g.*, crude benzol, 50/90 benzol, and so on. The recovery of benzol from coal-gas implies the extraction of vapours of the benzene series, and their subsequent conversion by condensation into various liquid products.

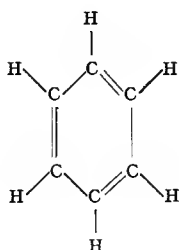
The benzene series is the most important group of substances in the class of Aromatic Hydrocarbons, the general formula of the series being  $C_nH_{2n-6}$ . The members of particular interest are the first three, benzene, toluene and xylene, which at normal temperatures are clear colourless liquids having very similar properties. The chief properties are given in *Table I* below :—

TABLE I.—PROPERTIES OF BENZENE AND ITS  
HOMOLOGUES.

HYDROCARBON.	Formula.	Specific gravity at 15.5° C.	Boiling point, ° C.	Freezing point, ° C.
Benzene .	$C_6H_6$	0.885	80.3	5.48
Toluene .	$C_7H_8$	0.870	110.8	— 90
Xylene .	$C_8H_{10}$	0.866—0.869	138.5—143	—

The constitutional formula now usually adopted for benzene is that of Kekulé who assumed that the structure of the molecule

corresponds to a closed ring of six carbon atoms, each united to its neighbours and to an atom of hydrogen, thus :—

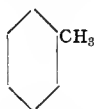


often written as :

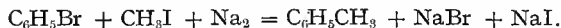


Applying this formula to the other members of the series it is clear that toluene may be regarded as methyl benzene, *i.e.*, benzene in each molecule of which an atom of hydrogen has been replaced by the methyl group,  $\text{CH}_3$ . Thus we may write the formula of toluene as :

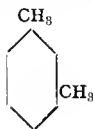
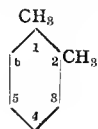
$\text{C}_6\text{H}_5 \cdot \text{CH}_3$ , or, graphically :



Experimental evidence is not lacking to support this theory, and toluene behaves chemically as methyl benzene. An example is its synthesis from bromo-benzene and methyl iodide :



Similarly, by applying the same reasoning to xylene this substance may be regarded as dimethyl benzene,  $\text{C}_6\text{H}_4(\text{CH}_3)_2$ , and this is also confirmed by experiment. On writing this formula graphically, however, it is clear that there are three possible arrangements of the molecule, thus :



There are, in fact, three isomeric xylenes, or substances of the composition and molecular weight corresponding to  $\text{C}_8\text{H}_{10}$ . The first, in which the methyl groups assume the 1.2 position, is known as ortho-xylene ; the 1.3 placing gives meta-xylene ; and the 1.4 compound is para-xylene. These three isomers differ slightly in properties, and xylene, as commonly produced, is a mixture of all three, meta-xylene usually predominating (*Table 2*).



TABLE 2.—THE ISOMERIC XYLENES.

XYLENE.	Position of CH <sub>3</sub> groups.	Specific gravity.	Boiling point, °C.	Melting point of solid, °C.
Ortho-xylene .	1.2	0.8682	142—143	— 28
Meta-xylene .	1.3	0.8691	139	— 54.8
Para-xylene .	1.4	0.8661	138.5	15

Benzene was first discovered in the year 1825 by Michael Faraday, who found it in the condensate obtained on compressing oil-gas. Toluene was recognised in 1838 in a similar condensate of resin-gas, and owes its name to its later preparation from tolu balsam. The uses of the benzene hydrocarbons, which will be briefly discussed later, are many. In addition to providing valuable solvents for greases and other organic substances, this series of compounds forms the starting point for the manufacture of the so-called "Coal Tar Dyes." This artificial dyestuff industry, originating in the discovery of mauve by Perkin in 1856, has now assumed a position of immense importance in the economic world. Synthetic chemistry has also given us many drugs, perfumes, etc., from the same source. For some years prior to the war mixtures of these hydrocarbons, in the form of various grades of benzol, were finding rapidly extending use as motor fuels in consequence of the steady increase in the price of petrol. There is no doubt, moreover, that very large quantities of benzol will be consumed for this purpose in the near future. It was the war itself, however, which brought home to us the importance of benzol, and almost from the beginning of hostilities there was an ever-increasing demand for its production. Practically every modern high explosive owes its origin to benzol and its associated compounds. The famous T.N.T. (trinitro-toluene) results from the nitration of toluene obtained from crude benzol. Picric acid, or "Lyddite," is produced indirectly from benzene, which is first converted into phenol. It will be seen, then, that the supply of benzol is of the utmost importance to the country whether in times of war or of peace. Consequently, it will be little short of a calamity if the interest caused by the stimulus of war-time demands is allowed to die down, instead of being applied to the continuation and extension of our benzol output for purposes such as motor fuel and synthetic organic products.

### Sources of Benzol

Benzene hydrocarbons occur to a varying extent in natural petroleum. During the war the richest of these, Borneo petroleum, was imported in large quantities. This crude oil contains

about 14—15 per cent. each of benzene, toluene and solvent naphtha, mixed with about 50 per cent. of paraffins. Although this oil proved a valuable source of toluene, it is difficult and expensive to obtain the pure hydrocarbons sufficiently free from paraffins to make them suitable for general use, and toluene from this source was replaced as far as possible by the purer hydrocarbon resulting from the carbonisation of coal.

Certain synthetic and catalytic processes have been suggested for the production of benzol, but do not yet appear to have advanced beyond the experimental stage. A more likely source of aromatic hydrocarbons is found in the thermal decomposition, or "cracking," of various petroleum oils. These crude oils contain paraffins, olefines and naphthenes which, when subjected to the effects of high temperatures and pressures, under controlled conditions, decompose into various aromatic hydrocarbons, benzene, toluene and xylene, as well as naphthalene, anthracene, etc. The diminishing supply of petrol directed attention to this process, and at least one large-scale plant is in operation in the United States, but the results from this installation have not been entirely satisfactory. Russian petroleum is more suitable for cracking than the American oil, owing to its higher naphthene content, and aromatic compounds for the production of dyes and explosives have for some time been obtained from it in the former country. Egloff, who has carried out much work on the subject, gives the following, among other, conclusions (*Met. and Chem. Eng.*, 1917):—

(1) All groups of paraffin hydrocarbons have formed benzene and toluene on the thermal treatment, with one exception, methane.

(2) The temperature of cracking may be so controlled as to give a maximum yield of benzene, toluene, naphthalene, or anthracene. The pressure and time-factor are important, but not to the same extent as the temperature.

(3) The group of paraffin hydrocarbons present in petroleum distillates is of great importance in forming aromatics in large yields.

### Benzol from Carburetted Water-Gas

The manufacture of carburetted water-gas is essentially an oil-cracking process, although the conditions as to temperature and atmosphere differ from, and are not under the same control as those in the methods mentioned above, in which the production of certain aromatics from the petroleum is the principal object in view, and where a crude oil, containing fractions both lighter and heavier than gas-oil, is used. Blue water-gas is enriched by passing it through the carburettor—a cylindrical vessel filled with chequer-bricks and maintained at about 750° C. Into the top of this chamber is sprayed the gas-oil fraction of petroleum, which is there vaporised and partly decomposed. The carburetted gas

then passes through a similar, but larger vessel called the superheater, the temperature of which is maintained around  $800^{\circ}\text{C.}$ , and in which the oil is finally cracked.

The benzol obtained by oil-washing carburetted water-gas is apt to contain an excess of paraffins and unsaturated bodies. Moore and Egloff extracted, per 1,000 cubic feet of gas, 0.32 gallon of light oil containing roughly 52 per cent. of benzol, 24 per cent. of toluol and 35 per cent. of unsaturated olefines. By increasing the temperature of the superheater, the proportion of the last-named impurity was reduced, and it would appear that with the temperatures usual in this country this difficulty does not arise. Applebee (*Proc. Junior Gas Associations*, 1916—17) found no increased washing difficulties when water-gas benzol was introduced and he gives the production as 2.5—2.8 gallons of crude spirit per 11,000 cubic feet of gas, the calorific value of which was reduced by about 6 per cent.; the proportion of oil used is not given. T. F. E. Rhead (*J. Soc. Chem. Ind.*, xxxvi., p. 767) obtained 3.27 per cent. of the original oil as benzene and about 2 per cent. as toluene, and these products were not seriously contaminated with paraffins. Hoffmann found that the impurities in a sample of water-gas toluene were less than 1 per cent.

It is of interest to note here some further experiments by Egloff, in which solvent naphtha was introduced into the carburettor in place of the usual gas-oil at the rate of 12 gallons per 1,000 cubic feet. With the superheater working at  $825^{\circ}\text{C.}$  the following products were obtained per 100 gallons of solvent naphtha cracked:—

	Gallons.
Refined benzol . . . . .	8.3
Refined toluol . . . . .	13.6
Refined solvent naphtha . . . . .	11.2
Crude heavy naphtha . . . . .	5.5
Dead oil . . . . .	8.0

### The Carbonisation of Coal

The most important source of aromatic hydrocarbons is the carbonisation of coal, and the presence of benzene in coal-tar was first recognised by Hoffmann in 1845. Toluene also occurs in tar, but from 20 to 40 times as much of both these hydrocarbons is found in the gas produced in the modern gasworks or coke-oven plant.

The mode of formation of these substances (which do not exist as such in the coal) during carbonisation is a matter of considerable doubt. Benzene was a few years ago generally supposed to result from the polymerisation of acetylene, three molecules of the latter gas coalescing to give one of the former. This theory, which was due to Berthelot, further assumed that the higher aromatics, *e.g.*, naphthalene and anthracene, were formed by the union of benzene with more acetylene. Since this theory was

formulated, however, the series of naphthenes or hexahydro-benzenes has been discovered, and it has been shown that, not only are these substances produced during the initial stages of carbonisation, but they also decompose under the influence of heat into the corresponding benzene compounds and hydrogen. Thus, hexahydrotoluene gives toluene and hydrogen :



Professor Bone has further shown that "acetylene never exists in any part of a gas retort in amounts sufficient to warrant its being regarded as the principal, much less the only, progenitor of the aromatic hydrocarbons." Acetylene is, however, formed in small quantities during carbonisation, and it has been found to polymerise at comparatively low temperatures. A consideration of the research of Armstrong and Miller on oil-gas manufacture, as well as of the results of the oil-cracking process, shows that benzene and toluene are also produced by the decomposition of olefines and paraffins. We may therefore conclude that the formation of benzene hydrocarbons during the carbonisation of coal is due to three groups of reactions :—

- (1) Dehydrogenation of corresponding naphthenes.
- (2) Decomposition of olefines and paraffins.
- (3) Polymerisation of acetylene.

Although in practice benzol recovery is more satisfactory when a comparatively high retort temperature is employed, it is interesting to note that benzene is practically a low-temperature product, though when recovered from a low temperature carbonisation process it is seriously contaminated with paraffins which have escaped decomposition. Recent research indicates that the maximum yield of benzene would be obtained at 700—750° C. Cobb and Hollings (*Trans. Inst. Gas Eng.*, 1914) have shown that, on passing 5 per cent. of benzene in a mixture of equal parts of methane and hydrogen through a hot tube, a temperature of 1,100° C. decomposed the whole of the benzene, which was untouched at 800° C. The question which arises is : Why is any benzene formed in a modern retort at 1,100°—1,150° C. ? It must be remembered that many of the primary products of carbonisation are hurried away from the coal without attaining a temperature approaching that of the retort walls (and, in fact, this accounts for the presence of paraffins in gas produced in a high-temperature retort). The influence of atmosphere must also be considered, and in this connection Cobb and Dufton (*Gas Journal*, cxlii., 482) have recently found that benzene, in an atmosphere of nitrogen, began to decompose at 550° C.

In view of the above results it would seem that much more benzene—and probably, also, its homologues—is formed in the retort than subsequently appears in the products of carbonisation. As it is, however, these products form the principal source of benzene compounds, which all occur in both tar and gas, the

quantities of each varying considerably with the class of coal and with the conditions of its carbonisation.

A normal coal-tar produced from horizontal retorts at a moderately high temperature contains, on an average, about 0.6—1.0 per cent. by volume of benzene, 0.3—0.5 per cent. of toluene, and 0.2—0.6 per cent. of xylenes. These hydrocarbons are recovered as crude naphtha and light oil during tar distillation.

### Benzol in Coal Gas

The quantity of benzene homologues in gas varies considerably with the treatment to which the gas has been subjected during manufacture, as well as with the class of coal, and the system and temperature of its carbonisation. If a high yield of benzol is desired, it is obviously unwise to keep the gas in contact with coal-tar for a prolonged period. Thus the available yield of benzol is dependent, to a certain extent, on the design of hydraulic main, condensers, etc. On the other hand, fairly drastic condensation is considered essential for the elimination of naphthalene. The class of coal carbonised has, however, a much greater influence on benzol recovery, and *Table 3* (which combines published results with the author's experience) will give an idea of the relative amounts of crude benzol in the gas produced under similar conditions of carbonisation.

TABLE 3.—APPROXIMATE YIELDS OF CRUDE BENZOL FROM DIFFERENT COALS.

COAL.	Gallons crude benzol per ton.
Yorkshire . . . . .	3 — 3½
Lancashire . . . . .	2½ — 3½
Durham . . . . .	2½ — 3
Midland and N. Wales . .	2½ — 2¾
Cumberland . . . . .	2½ — 2¾
Somerset . . . . .	1½ — 2
Scottish * . . . . .	1½ — 2
S. Wales . . . . .	1 — 1½

\* Some Scottish coals contain shale, and these give paraffinoid benzols.

The conditions of carbonisation are of fundamental importance as regards both the quality and quantity of benzol produced per ton of coal. It has been seen that the primary products of distillation are largely composed of paraffins and olefines, which, on heating, are decomposed—to a greater or lesser extent, depending on temperature, time-contact, atmosphere, etc.—to give members of the benzene series and other aromatics. On

further cracking there is a tendency for the higher benzenes to break down, giving benzene itself, and also two-ring or three-ring hydrocarbons, such as naphthalene and anthracene. Thus, from a given coal, a lightly charged horizontal retort at a moderately high temperature gives a benzol rich in benzene and almost free from paraffins, whilst the gas contains also a considerable amount of naphthalene. The same coal carbonised in continuous vertical retorts—which give virtually low-temperature distillation—would yield a smaller quantity of benzol per ton, in which paraffin would appear and the proportion of benzene to its higher homologues would be lower. A “packed” horizontal retort gives conditions approximating to those in the vertical plant; but coke-oven benzol is very similar in composition to that produced from horizontals, owing to the less rapid evolution of the gas from a greater bulk of (usually wet) coal. Inclined retorts give results intermediate between those from horizontals and verticals, probably owing to the comparatively low temperature of the bottom of the retort, where the off-take pipe is situated. These expected variations are found in practice, as is shown by *Table 4*. This gives the average analysis of a large number of samples of crude benzol from all parts of the country. For purposes of comparison the composition has, in each case, been corrected to the same “wash-oil content,” *i.e.*, residue above 170° C.

TABLE 4.—AVERAGE ANALYSIS OF CRUDE BENZOLS FROM DIFFERENT CARBONISING SYSTEMS.

RETORTS.	Specific gravity.	Paraf. fins.	Ben- zene.	Toluene.	Xylene.	Loss on washing.	Residue above 170° C.
Horizontal .	·896	1·3	50·3	16·4	8·0	5·8	17·7
Inclined .	·875	5·3	32·5	18·0	13·7	12·5	17·7
Vertical .	·860	12·6	26·7	11·5	20·1	11·0	17·7

As regards quantity of benzol, this does not appear to vary very considerably in this respect. The order of importance of the various types of carbonising plant is roughly : horizontal retorts, coke-ovens, inclined retorts, intermittent vertical retorts,, continuous vertical retorts.

### The Recovery of Benzol from Gas

One of the earliest suggestions for the removal of benzol from gas entailed compression of the gas at a low temperature. Such a process of refrigeration is obviously impracticable where such large volumes of gas must be treated for a relatively small yield of condensate. A. Vogel used colza oil for the absorption of benzol from gas, whilst Caro, in 1869, proposed the use of high-boiling

petroleums, or other heavy oils. But the market value of benzol soon declined and the process was discontinued until the rise in price (due to the demands of the dye industry) again revived interest in the subject. The oil-washing process was then developed, and its adoption has gradually extended until, at the present time, most of the coke-oven plants in this country are equipped for its operation. The Gas Light and Coke Company introduced oil-washing in their gasworks before 1914, but, owing chiefly to restrictive legislation, it required the demands of war to effect the adoption of the process by the gas industry in general.

### The "C" Process

In 1887, Friedländer and Quaglio patented the use of thin tar as a substitute for wash-oil, and early in the war period Dr. C. C. Carpenter drew the attention of the Ministry of Munitions to this, which became known as the "C" process. Tar washing was thereupon brought into operation in the majority of gasworks throughout the country, and by this means the benzene and toluene contents of the tar produced were approximately doubled. The advantage of this method was its ease and rapidity of application in existing plant; its chief drawbacks were the necessity of using tar as free from water as possible, the difficulty of keeping down the washing temperature, possible addition of naphthalene to the gas, and, above all, the limited recovery due to the fact that the amount of tar available for washing was restricted to the quantity made. The benzene and toluene were recovered during the subsequent distillation of the tar in the ordinary course.

### The Oil-washing Process outlined

The method now universally adopted for the extraction of benzol from gas is the oil-washing process. This depends on the fact that a heavy hydrocarbon, or mixture of hydrocarbons, such as creosote or heavy petroleum oils, will readily dissolve benzene and its homologues, which may be obtained out of solution by simple distillation, both solvent and solute being practically unchanged in the process. Other constituents of coal-gas also dissolve in the oil and are similarly removed, to appear as impurities in the crude benzol.

In practice the gas is washed or scrubbed in a suitable form of apparatus with such a quantity of oil as will give effective absorption, the scrubber being situated at a point where the gas is as cool, and as completely purified as possible. FIG. 1 shows diagrammatically the arrangement of the plant.

The benzolised oil leaving the scrubber is passed through heat exchangers and preheaters of various designs until its temperature is raised to about 120° C. By this time some of the dissolved benzol is removed, and the remainder is abstracted by the

subsequent passage of the hot oil through a still, where it meets a current of steam. The benzol vapours and steam pass together through a condenser, and finally as liquids to the separator. Here the condensed water and benzol are divided, the latter flowing to the storage tank. The debenzolised oil leaving the still flows through the heat exchanger, where economy is effected by the transference of some of its sensible heat to the cold ingoing oil, and thence through coolers to the debenzolised oil tank.

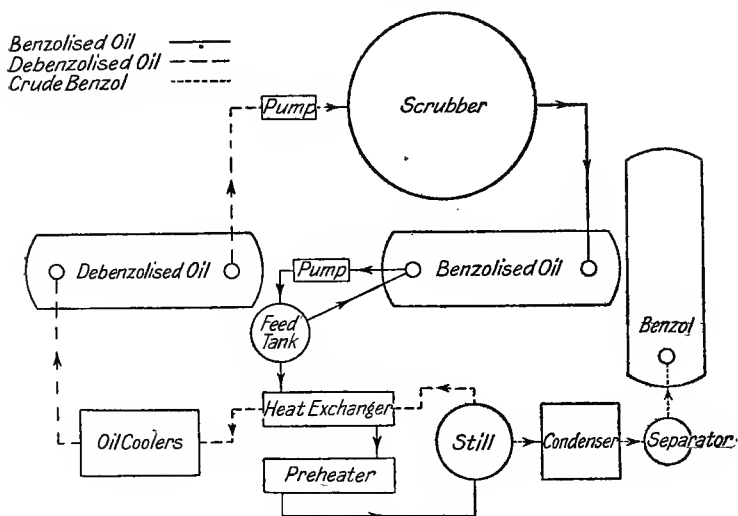


FIG. 1.—DIAGRAMMATIC ARRANGEMENT OF CRUDE BENZOL PLANT.

From here it is again pumped over the scrubbers, where it meets a fresh volume of gas, the cycle being completed time after time.

### The Effect of Oil Washing on the Gas

The effects of benzol extraction on the gas may be subdivided into :

- (1) Reduction in gas volume.
- (2) Loss of illuminating and calorific power.
- (3) Effect on flame temperature and flame volume.
- (4) Alteration in specific gravity and composition of the gas.

#### *Reduction in Gas Volume*

The volume of 1 gallon of pure benzene when vaporised at normal temperature and pressure is, roughly, 40 cubic feet. Crude benzol is mainly composed of benzene and its homologues of progressively higher boiling point and molecular weight. The gaseous volume of 1 gallon of these homologues decreases as the



hydrocarbons become heavier, as shown by the calculated results in *Table 5*.

TABLE 5.—GASEOUS VOLUME OF HYDROCARBONS.

HYDROCARBON.	Formula.	Molecular weight.	Boiling point, ° C., approximate.	Specific gravity of liquid.	Cubic feet vapour per gallon liquid.
Benzene .	$C_6H_6$	78	80	0.885	40.7
Toluene .	$C_7H_8$	92	111	0.870	33.9
Xylene .	$C_8H_{10}$	106	139	0.866	29.3

Consider a crude benzol containing 55 per cent. of benzene, 15 per cent. of toluene and 10 per cent. of xylene. These hydrocarbons removed from the gas represent only 30.4 cubic feet of vapour for every 1 gallon of crude benzol made. To this must be added the gaseous volume of the impurities derived from the gas. These consist of carbon disulphide, paraffins, naphthalene and unsaturated bodies, to the extent of 5—8 per cent. of the benzol, and their volume in the gas is comparatively small. We see, therefore, that the removal of 3 gallons of average crude benzol per 12,000 cubic feet of gas causes a reduction in volume of something less than 1 per cent. Edwards gives this figure as "about 1 per cent.," while Schaeffer states that the gaseous volume of crude benzol is 35 cubic feet per gallon, which also corresponds with about 1 per cent. for the rate of recovery stated.

#### *Loss in Calorific Value*

The reduction in calorific value of the gas varies with the composition of the benzol and with other factors. It may be taken that the recovery of 1 gallon of average 65's crude benzol per ton of coal causes a reduction of 12—14 B.Th.U. per cubic foot gross. This figure, which agrees with theory, has been verified time after time by the author's experiments, and has also been confirmed by other workers. A. Edwards states that the recovery of 3 gallons of crude benzol per ton of coal reduces the calorific power of the gas by 35 B.Th.U., and Alwyne Meade (*Proc. Inst. C. E.*, 1917) gives the following interesting table (*Table 6*) :—

TABLE 6.—REDUCTION IN CALORIFIC VALUE OF GAS BY EXTRACTION OF BENZOL.

Gallons crude benzol per ton of coal.	Loss in calorific value of gas, per cent.
2.1	4.5
2.5	7.0
3.0	8.0

From the point of view of theory, the calorific values of the principal constituents of benzol are roughly as in *Table 7* :—

TABLE 7.—CALORIFIC VALUES OF CONSTITUENTS OF BENZOL.

CONSTITUENT.	B.T.H.U. PER GALLON.	
	Gross.	Nett.
Benzene .	163,000	160,000
Toluene .	152,000	148,800
Xylene .	141,000	137,700

Thus the gross calorific value of 3 gallons of crude benzol of the composition given on p. 11 would be 379,800 B.Th.U. The recovery of this quantity per 12,000 cubic feet of gas would therefore effect a reduction of 31·65 B.Th.U. gross per cubic foot, plus the thermal value of the paraffins and other impurities extracted, which agrees closely with the reduction found in practice.

#### *Reduction in Illuminating Power*

A normal coal-gas of 15—16 c.p. contains about 3 per cent. by volume of heavy hydrocarbons or “illuminants.” Roughly one-third of this amount is extracted when 3 gallons of crude benzol are recovered per ton of coal. It will, therefore, be apparent that the reduction in the illuminating power of the gas will be very marked, and, in fact, one of the chief uses of benzol a few years ago was as an enriching agent for bringing the candle power of gas up to the old-fashioned statutory requirements. The substitution of calorific standards in many cases, and the almost universal adoption of the incandescent burner instead of the flat-flame type, have rendered the illuminating power of gas a subject of very little importance, and there is no doubt that in the near future this property of gas will be a matter of scientific interest only. Whilst the candle power of the gas in no way affects the incandescent burner (the efficiency of which depends entirely on flame temperature, flame volume and specific gravity), it is of interest to know that the recovery of 3 gallons of crude benzol per 12,000 cubic feet will reduce the illuminating power of a 16-candle gas (No. 2 Argand) to about 9—10 c.p. When it is remembered that the luminosity of a flame is derived from incandescent particles of carbon, and that 3 gallons of crude benzol represent nearly 11 per cent. of the total carbon content of 12,000 cubic feet of gas, this relatively large loss of candle power will be understood, for not only is a large proportion of the carbon particles removed, but the amount of air necessary for their

combustion is still present and this results in the more rapid disappearance of the remaining carbon.

Flat flame burners, designed for the use of "stripped" gas, are now on the market; the gas issues from a larger orifice at a lower velocity, and consequently gives less rapid combustion by reducing the amount of air drawn into the flame. In this way an increased duty is obtained.

### *Effect on Flame Temperature and Flame Volume*

The amount of radiation emitted by an incandescent body is proportional to the fourth power of its absolute temperature. The question of flame temperature is, therefore, of vital importance in the use of incandescent burners, as well as of other appliances—such as gas fires—the efficiency of which depends on radiation.

No method is available for the direct measurement of relative flame temperatures, but a useful indication is the theoretical maximum, or calculated flame temperature. This is closely allied to the question of combustivity, or volume of air required for the complete combustion of unit volume of gas, which is considerably greater for the "illuminants" than for the other constituents of the gas. The theoretical flame temperature of an average coal-gas and air is from  $2,300^{\circ}$  to  $2,400^{\circ}$  C. In spite of its much higher calorific value (3,570 B.Th.U. nett per cubic foot) benzene vapour has a flame temperature of only  $2,525^{\circ}$  C. when burnt with the theoretical minimum of air. That of toluene is less owing to its lower thermal value and greater combustivity, whilst xylene gives a yet cooler flame. It is, therefore, clear that the removal of benzol from gas will not appreciably reduce its theoretical flame temperature, and a reference to *Table 8* shows that, with the particular gas there given, this value is actually increased by the process of recovery. At the same time the flame volume is affected to only a very slight extent. It may, therefore, be accepted that "stripped" gas is in practice as effective in incandescent appliances, both burners and fires, as unstripped gas. In the author's experience the oil-washing of very rich gases has, in a number of cases, brought about a marked improvement in the incandescent lighting of the district supplied.

### *Specific Gravity and Composition of the Gas*

As the density of benzol vapour is some five or six times that of an average coal gas, the removal of 1 per cent. of the former will appreciably reduce the specific gravity of the gas. Such a reduction is a distinct advantage from the distributing engineer's point of view, and, moreover, a stripped gas is much more constant in quality than a rich one owing to its being less liable to condensation in the mains, with subsequent re-evaporation in

# BENZOL

TABLE 8.—EFFECTS OF BENZOL RECOVERY ON A NORMAL COAL-GAS.

Gallons crude benzol recovered per ton of coal.	Gas volume, cubic feet per ton of coal.	Analysis of gas, per cent.*						Specific gravity of gas. Air = 1.	Illuminating power, No. II. approximate.	Calorific value, B.Th.U. per cubic foot.		Com-bur- vity, cubic feet air per cubic foot gas.	Rela- tive flame volume	Theo- retical flame tempera- ture, °C.	Impurities, grains per 100 cubic feet.	
		CO <sub>2</sub> .	C <sub>2</sub> H <sub>2</sub> m.	O <sub>2</sub>	CO.	CH <sub>4</sub> .	H <sub>2</sub> .	N.		Gross.	Nett.				S.	C <sub>10</sub> H <sub>8</sub> .†
<i>Nil.</i>	12,000	2.00	3.00	1.00	9.00	28.00	49.00	8.00	15½	536	484	4.91	1.07	2,360	40	6
1½	11,950	2.01	2.50	1.00	9.05	28.13	49.26	8.05	12½	519	468	4.72	1.04	2,363	30-33	2
3	11,900	2.02	2.00	1.01	9.10	28.25	49.52	8.10	9½	503	452	4.54	1.00	2,366	26-28	1

\* The solution of permanent gases is ignored. Effect practically negligible.

† Approximate only and depends on working of debenzolising plant. (See Chapter VII.)

warmer weather. This effect has been very noticeable in connection with the stripping of "gasoline" from natural gas in the United States.

As regards the composition of the gas, the removal of 1 per cent. of heavy hydrocarbons has otherwise but little effect on the analysis. The wash-oil probably absorbs a small amount of permanent gases, but no figures are available as to this; their volume, however, is certainly negligible.

In some works oil-washing is carried out on crude gas, and there a portion of the hydrogen sulphide is absorbed by the oil, together with any traces of ammonia (subsequently recovered at the separator) and some of the cyanogen compounds. But, whatever the position of the oil washer, the most important effect on the composition of the gas concerns its content of naphthalene and organic sulphur compounds.

With very little trouble a benzol washer may also be worked as a naphthalene extractor; this subject is discussed fully in Chapter VII. As regards sulphur compounds (other than hydrogen sulphide) these are usually reduced in the oil washer by some 10—20 grains of sulphur per 100 cubic feet of gas, the sulphur reappearing as carbon disulphide, thiophene, thiotolene, etc., in the crude benzol.

The effects of oil-washing on the gas, which are summarised in Table 8, are, therefore, practically negligible—and, indeed, are rather advantageous than otherwise—with the exception of the reduction in calorific value. The universal tendency for some years has been towards a lower grade of gas, and in view of the preliminary report of the Gas Investigation Committee of the Institution of Gas Engineers, this reduction cannot be considered an objection to the general introduction of benzol recovery. This report shows that, in ring burners, upright incandescent burners and gas fires, it is possible to vary the calorific value of the gas within wide limits without impairing the efficiency of its utilisation. For apparatus which depends upon the *quantity* of heat used, *e.g.*, gas engines, ovens, etc., it should be only necessary to use some 5—7 per cent. more stripped gas for the same operation. On the other hand, when the use of an appliance depends upon thermal *intensity*, as in incandescent burners, gas fires and some furnaces, stripped gas would appear to be as efficient as, if not actually more efficient than the richer unwashed gas.

### Reasons for general Adoption of the Process

When gas is sold at 5s. per 1,000 cubic feet the value of 1 gallon of crude benzol sold as gas is 2d. In the liquid form (rectified) the price obtainable for the same quantity is, to-day, about 3s. 3d. per gallon, and with the greater use of benzol for motors there is every prospect of a considerable increase in its value. There is, moreover, little fear of reducing the market price by

over-production because if all the available benzol in the country were recovered it would not be sufficient to meet the whole of the demand for motor fuel alone. These facts, coupled with the absolute necessity for the greater development of the nation's fuel resources, should be sufficient to cause the general adoption of benzol recovery throughout the gas industry. Whether oil-washing can be made thoroughly successful under an antiquated standard of illuminating power is, however, open to doubt ; and for this as well as for other urgent reasons, every effort should be made to bring about the general application of statutory control on a calorific basis.

## CHAPTER II

### THEORETICAL PRINCIPLES

ALTHOUGH benzol recovery is a comparatively simple process, the theory of the subject is complicated, but at the same time extremely interesting. It depends almost entirely upon considerations of vapour pressure. The molecules which constitute all matter are in a state of perpetual motion. Those of a solid have a high power of mutual attraction. When the solid is liquefied this power of attraction is lessened, and the molecules attain increased mobility or freedom of movement. The same change—but to a greater degree—takes place when a liquid is converted into a vapour, and in that state the molecules are in a condition of high mobility and move with a considerable velocity. For this reason, a gas introduced into a closed space will immediately diffuse through, or permeate, the whole of that space. The kinetic theory further tells us that the pressure of a gas is due to the continual collision of its particles with the walls of the containing vessel, and since increased temperature brings about greater velocity, it also results in an increase of pressure. In the case of a vapour in an enclosed space in contact with its liquid, this pressure, which is known as vapour pressure or vapour tension, has a definite value for a given liquid and temperature. This value, which is expressed in millimetres of mercury column, therefore varies with the temperature; but, on account of the property of diffusion, is independent of the size and shape of the containing vessel so long as any of the liquid is present. If more than one liquid be present, the vapour tension of each is known as its partial pressure, and when the liquids are neither miscible nor chemically related—water and benzene, for example—the partial pressure of each is equal to the pressure which its vapour would exert if it alone were present, and at the same temperature; that is, the total vapour pressure is equal to the sum of their separate vapour pressures at that temperature. On the other hand, liquids which mix give a smaller total pressure.

#### Vapour Pressures of Mixtures

In the case of a mixture of two liquids which are miscible and chemically related—e.g., benzene and toluene—some doubt exists as to the total pressure exerted, and the matter is fully discussed by Young in his book *Fractional Distillation*. The

theory of Guthrie states that the partial pressure of each constituent is proportional to the percentage present *by weight*, and Speyer concludes that this partial pressure is proportional to the *molecular* percentage of the constituent in the mixture. The latter would certainly be true if no molecular association took place on mixing; and, in fact, it appears that Speyer's theory is the more probable one in connection with solutions of benzols in creosote, for it has been shown that closely related liquids give observed pressures very nearly in agreement with those calculated by this theory. Accordingly the total vapour pressure,  $P$ , of such a mixture at any particular temperature is found by the following formula :—

$$P = \frac{M_A}{100} P_A + \frac{100 - M_A}{100} P_B,$$

where  $P_A, P_B$ , are the separate vapour pressures of liquids A and B respectively at the same temperature, and  $M_A$  is the molecular percentage of liquid A in the mixture.

### Solution of a Gas in a Liquid

When a gas which is soluble in a liquid is brought into contact with it, some of its molecules are continually colliding with the surface of the solvent. These enter the liquid, and are held in solution in consequence of the attraction between themselves and the molecules of the solvent. They are, however, still in a state of motion, and some of them in turn leave the solution and re-enter the gas. This process continues until the number of molecules of the solute leaving the liquid per unit of time is equal to the number entering it, and the gas and its solution are then said to be in a state of equilibrium. Beyond that condition, which also varies with the temperature, the concentration of the solution will not increase, or in other words, the liquid is saturated with the particular gas for that temperature and vapour pressure of the solute. If the latter is one of a mixture of gases, then, the only means by which more can be made to dissolve is either by increasing its partial pressure in the gaseous mixture, or by introducing more solvent and so reducing the vapour pressure of the solution. This obviously has an important bearing on the recovery of benzol from gas.

### Partial Pressures

The partial pressure of a constituent forming  $x$  per cent. by volume of a mixture of gases is  $760 \times \frac{x}{100}$  mm. In coal-gas containing 0.8 per cent. of benzene vapour, therefore, the partial pressure of the latter would be  $\frac{760 \times 0.8}{100} = 6.08$  mm. For



practical purposes it may be taken that the vapour pressure of creosote at ordinary temperatures is *nil*, and the tension of benzene vapour at 15° C. is 58 mm. Substituting in the above formula we find that the molecular percentage of benzene in the mixture,

$$M_A = \frac{6.08 \times 100}{58} = 10.5 \text{ per cent.}$$

Taking the molecular weight of creosote as 153 (which corresponds to  $C_{12}H_9$ ) and its specific gravity as 1.2, this gives the percentage of benzene in the solution as 7.3 per cent. by volume. In other

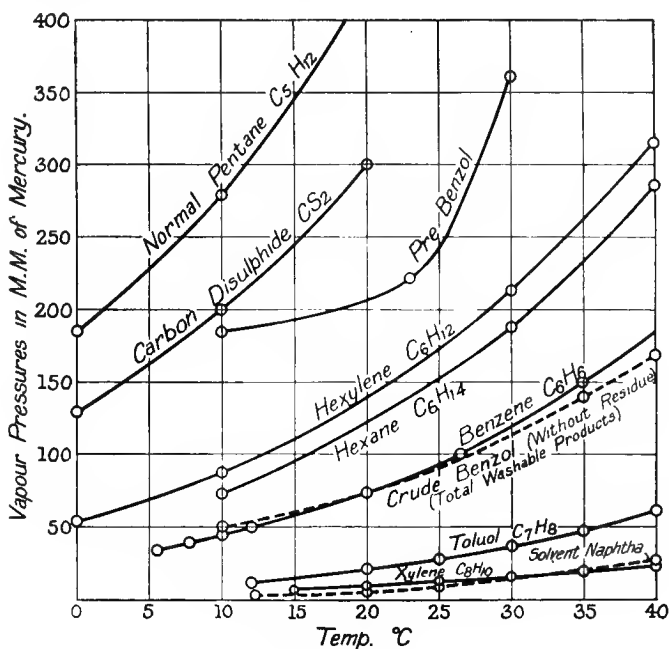


FIG. 2.—VAPOUR PRESSURE OF LIQUIDS.

words a 7.3 per cent. solution of benzene in creosote is in equilibrium with a gas containing 0.8 per cent. of benzene vapour at a temperature of 15° C. This quantity of benzene in gas corresponds to 2.36 gallons per 12,000 cubic feet, and, given perfect washing conditions, the whole of the benzene would be extracted at that temperature by the use of 32 gallons of creosote per 12,000 cubic feet. Such conditions are, however, far from attainable in practice.

By the use of the curves given in FIG. 2, similar calculations may be made for other temperatures and vapours, and it is

possible to calculate the partial pressure in the gas of each constituent of the crude benzol, as also the amount of each which would be required to saturate the gas at any given temperature. T. F. E. Rhead (*Proc. Junior Gas Assoc.*, 1916-17) gives the following figures (*Table 9*) for a normal coal-gas, giving 3 gallons of washable benzols per 12,000 cubic feet, and for a gas saturated at 15° C. with each constituent separately.\*

TABLE 9.—BENZOLS IN NORMAL AND SATURATED COAL-GAS.

PRODUCT.	NORMAL COAL-GAS.				COAL-GAS, SATURATED AT 15° C.		
	Gallons per 12,000 cubic feet.	Percentage of whole.	Percentage by volume in gas.	Partial pressure, mm. Hg.	Percentage by volume in gas.	Partial pressure, mm. Hg.	Gallons per 12,000 cubic feet.
Pre-benzol . .	0.06	2	0.022	0.165	25.6	195	71
Benzol . . .	2.16	72	0.773	5.880	8.0	60	22
Toluol . . .	0.51	17	0.152	1.158	1.84	14	6.16
Solvent naphtha	0.27	9	0.069	0.528	0.53	4	2.04
Total . . .	3.00	100	1.016	7.731	35.97	273	101.2

\* NOTE.—These figures for the amount of hydrocarbons required to saturate a gas at 15° C. would probably not be strictly true if all the constituents were present, owing to the close chemical relation of these constituents. This follows from the vapour pressure of chemically related mixtures.

### Application to Oil Washing

By similar calculations to the above it is possible to find the amount of benzene in creosote theoretically required to be in equilibrium with a gas containing any given percentage of benzene vapour, and at any desired temperature. In this way the curves in FIG. 3 have been plotted.

FIG. 3, A, shows the percentages of benzene in creosote which are in equilibrium with certain proportions of benzene in gas at different temperatures. FIG. 3, B, gives similar creosote saturations for certain fixed temperatures, and with varying benzene content of the gas. The latter set of curves may be used to compare the effects of a certain recovery on the benzene content of the gas and on the saturation of the creosote, when using the theoretical minimum quantity of the latter. In both sets of curves the vapour pressure of creosote is assumed to be *nil*, the

error thus introduced being practically negligible. This fact results in straight lines in FIG. 3, B. In other words, the benzene content of the gas is proportional to the benzene saturation of creosote in equilibrium with it at any specified temperature. This follows from the question discussed on p. 19, for when equilibrium is reached the respective partial pressures of the benzene are equal. Thus, at  $t^\circ \text{C.}$ ,

$$\frac{M_B}{100} P_B = \frac{x_B}{100} \times 760$$

$$\therefore \frac{x_B}{M_B} = \frac{P_B}{760} = \text{a constant},$$

where the gas contains  $x_B$  per cent. by volume of benzene vapour ;

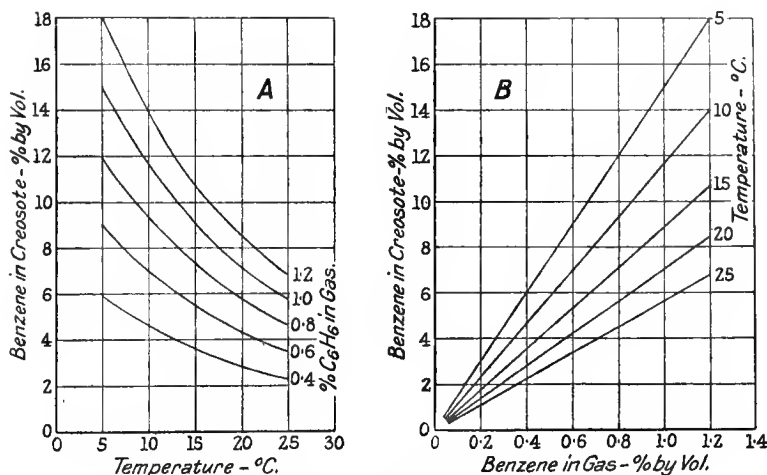


FIG. 3.—EQUILIBRIUM BETWEEN BENZENE IN GAS AND CREOSOTE.

$M_B$  is the molecular percentage of benzene in creosote ; and  $P_B$ , the vapour pressure of benzene at  $t^\circ \text{C.}$ , is constant for that temperature.

As an example, a gas containing 0.8 per cent. of benzene vapour is in equilibrium at  $20^\circ \text{C.}$  with creosote containing 5.7 per cent. of benzene by volume. It is not necessary to consider toluene, since the amount of creosote required to extract all the benzene is more than sufficient to remove the whole of the toluene, owing to the lower vapour tension of the latter and its smaller partial pressure in the gas. This is the case to a still greater extent with xylene.

Let us now consider a single chamber of creosote oil at  $20^\circ \text{C.}$ , through which is continually passing coal-gas containing benzene to the extent of 0.8 per cent. by volume, or 2.36 gallons per

12,000 cubic feet. Benzene is absorbed by the creosote until the strength of the solution reaches 5·7 per cent. After that point the gas retains the whole of its benzene, for this represents the strongest solution of benzene obtainable under the given conditions. In other words, the minimum quantity of creosote which must be used to give complete extraction of the benzene at 20° C. is  $\frac{2\cdot36 \times 100}{5\cdot7} = 41\cdot5$  gallons per 12,000 cubic feet.

If, however, 41·5 gallons of fresh creosote were added to the chamber for every 12,000 cubic feet we get the same condition as in a closed vessel containing this amount of gas and creosote. It is obvious that complete recovery would even now be unattainable, for as the benzene dissolves in the oil, its partial pressure in the gas is correspondingly reduced, so that when equilibrium exists, the gas still contains some benzene, whilst the saturation of the creosote is considerably less than 5·7 per cent., the

TABLE 10.—EFFECT OF CHAMBERS IN WASHER ON RECOVERY OF BENZOL.

NO. OF CHAMBERS IN WASHER.	PERCENTAGE RECOVERY.
1	50
2	75
3	87·5
4	93·75
Infinite.	100

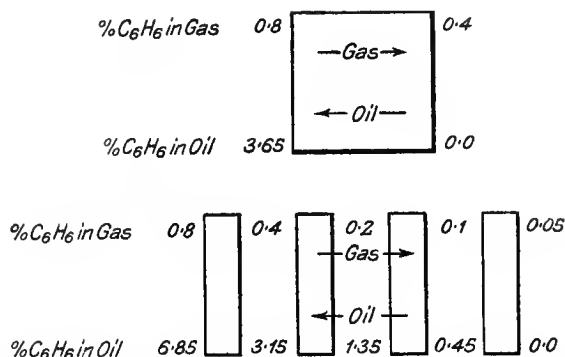
theoretical maximum. From FIG. 3, B, it will be seen that at 20° C., 0·4 per cent. of benzene in gas exerts the same partial pressure as 2·85 per cent. of benzene in creosote, and this is evidently the state of equilibrium under the conditions we are considering. Thus, if gas be washed with the theoretical minimum quantity of creosote in a single-chamber washer, only one-half of its benzene content can be removed by the oil. A higher rate of recovery may, of course, be obtained by increasing the proportion of creosote to gas washed, but this can be done only within certain limits, dependent largely upon the economical working of the debenzolising plant.

If, however, the gas passes into another chamber and there meets fresh creosote, the benzol recovered in the second chamber is again one-half of that contained in the gas entering it, and the total recovery is now three-quarters of the benzene content of the original gas. Similarly, by still further additions to the number of chambers, the total efficiency of extraction may be considerably increased, *provided that the course of the gas through*

the chambers is opposed to that of the oil. If the gas and creosote were allowed to flow through any number of chambers in the same direction, the effect would evidently be little better than their passage through a correspondingly large single chamber. The effect of increasing the number of washing chambers, whilst using the same amount of oil, is shown in *Table 10*.

The application of this principle to a concrete example is given diagrammatically in *FIG. 4*, which shows the benzene contents of gas and oil passing, counter-current, through washers of (a) a single bay, (b) four bays.

The values there given have been calculated from the curve



*FIG. 4.*—ABSORPTION OF BENZENE IN SINGLE-BAY AND FOUR-BAY WASHERS AT 15° C.

given in *FIG. 3, B*, for a temperature of 15° C., and assuming that the theoretical minimum of wash-oil is in use.

In a similar way *Table II* has been constructed for a gas containing 0.8 per cent. of benzene vapour (2.36 gallons per 12,000 cubic feet) under the same conditions of temperature and wash-oil supply.

*TABLE II.*—THEORETICAL WASHING EFFICIENCIES.

No. of bays.	Efficiency of washing, per cent.	Yield, gallons per 12,000 cubic feet.	Benzene saturation of oil, per cent.
1	50	1.18	3.65
2	75	1.77	5.47
4	93.75	2.21	6.85
6	98.44	2.32	7.18
Infinite.	100	2.36	7.30

It is, therefore, abundantly clear that benzol-washing must be

performed on the counter-current system, for by no other method are economy and efficiency to be attained.

It is interesting to note that complete recovery can never be accomplished in practice, and that it is only theoretically made possible by the use of either an infinitely large volume of oil or an infinite number of washing chambers. It is now easy to see the reason for the low efficiency of such a washer as a Livesey, as compared with that of an eight-bay rotary washer or high tower-scrubber. Even in the latter forms of plant, however, the theoretical recovery is never reached. The main reasons for this are, firstly, the time-contact between vapour and liquid is never sufficiently long, and secondly, the mechanical efficiency of the washer is always less than 100 per cent., owing to such factors as "slip" in a rotary machine or uneven distribution in the tower. Moreover, the wash-oil returned to the scrubber is never completely debenzolised. Edwards has obtained from 75 to 88 per cent. efficiency of extraction in a rotary washer of eight bays, and on this account he recommends the use of from 1.1 to 1.5 times the theoretical quantity of wash-oil. The question of time contact is an important one. Some tests carried out by the author on a tower scrubber, and using increasing quantities of oil per ton, showed that for the particular scrubber in use, maximum recovery was obtained with a circulation of only 55 gallons of oil per ton. At that rate of oil flow the yield of crude benzol was 3.1 gallons per ton of coal, and on increasing the supply of wash-oil to 79 gallons there was an actual fall in the recovery to 2.83 gallons of crude.

### Effect of Temperature on Scrubbing

A reference to FIG. 3 will make it almost superfluous to emphasise the importance of keeping the scrubbing temperature as low as possible, consistent with other factors. The chief of these is the viscosity of the wash-oil, which, as will be seen later, is also of vital importance. As the temperature of creosote falls it becomes more viscous, and this effect is more marked below 20° C. than above it, so that, despite the equilibrium curves, a reduced recovery may result from washing the gas much below that temperature. Another reason for maintaining a moderate temperature is that whilst warm oil has a tendency to give up naphthalene to the gas, yet an oil which is much cooler than the gas will cause the condensation of water vapour in the scrubber with consequent difficulties in working. Practical experience indicates that the best conditions are reached when the gas temperature is as near to 60° F. as possible, and the temperature of the wash-oil some 2° or 3° F. higher. It will be apparent from the curves of FIG. 3 that, in cases where it is impossible to cool the oil sufficiently (through lack of water or weather conditions) the loss in efficiency may be, to a certain extent, counterbalanced

by increasing the amount of wash-oil in circulation. Thus, whilst at  $15^{\circ}\text{C.}$  a gas containing 0.8 per cent. of benzene can theoretically be stripped by the use of 32 gallons of creosote per ton, the same effect can only be produced with 51 gallons at  $25^{\circ}\text{C.}$  This cannot be applied in every case, however, as the same increase also throws more work on the already inefficient coolers, and so results in still warmer oil.

### Effect of Over-saturation

The question now arises as to the effect of reducing the oil flow through the washing system per unit volume of gas. At first sight it might appear that reducing the amount of wash-oil used by 50 per cent. would merely halve the crude benzol recovered. Consideration of vapour pressures will, however, show this to be incorrect. By previous methods of calculation the following figures, all relating to  $15^{\circ}\text{C.}$ , are obtained :—

TABLE 12.—EFFECT OF OVER-SATURATION ON RECOVERY.

HYDROCARBON.	Percentage in gas by volume.	Vapour pressure at $15^{\circ}\text{C.}$ Mm.	Partial pressure in gas. Mm.	Percentage by volume in creosote in equilibrium.
Benzene .	0.8	58	6.1	7.3
Toluene .	0.2	15	1.5	8.3
Xylene .	0.1	8	0.8	9.7

Thus the effect of over-saturation of the oil will be a tendency for the composition of the crude benzol to approach the proportions given in the last column of *Table 12*, whereas the use of the requisite amount of oil to give complete stripping of the gas would result in a product of the proportions shown in column 2.

It is evident that to increase the toluene : benzene ratio in the creosote beyond that existing in the gas, considerable quantities of benzene must be carried forward unabsorbed. The same applies to the xylene : toluene ratio, so that, whereas complete stripping was formerly obtained, the result of over-saturation is to reduce the total output of crude spirit, the character of which becomes heavier as the degree of saturation of the oil increases. In other words, an over-saturated oil will absorb xylene whilst passing forward most of the benzene and some of the toluene. In practice, owing probably to the reduced proportion of absorbent in the saturated wash-oil, the yield of each constituent appears to drop after a time. These points are demonstrated by *FIG. 5*, which gives the results of some experiments performed by the author.

Redistilled gas-oil was circulated repeatedly over a tower-scrubber at the rate of 65 gallons per ton of coal, the gas passing at a speed of 75,000 cubic feet per hour. At the end of every hour a sample was distilled, and the light oil obtained was dried and fractionated. The increases in benzol, toluol and xylol contents were indicated roughly by the following fractions: Up to  $100^{\circ}\text{C}$ .,  $100^{\circ}\text{--}120^{\circ}\text{C}$ ., and  $120^{\circ}\text{--}145^{\circ}\text{C}$ . These fractions.

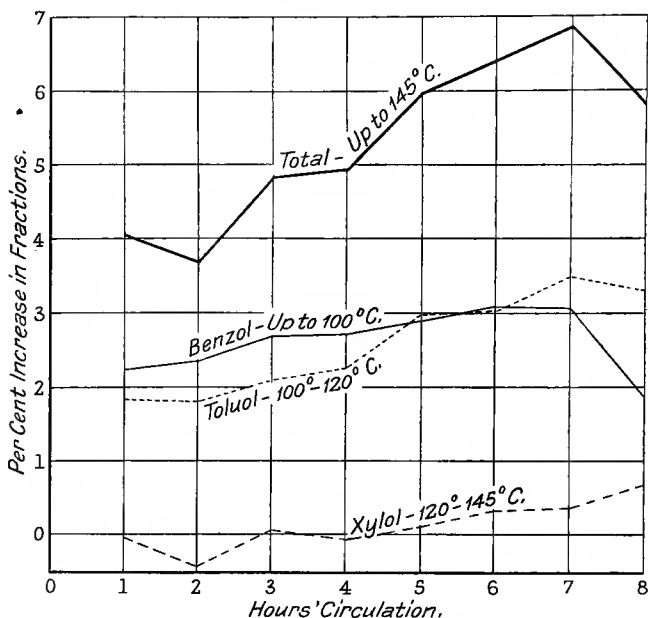


FIG. 5.—SATURATION TEST ON GAS-OIL.

together with the total distillate up to  $145^{\circ}\text{C}$ ., are plotted in FIG. 5.

### The "B" Process

A very interesting application of these effects is found in the "B" process, which was developed in 1915 by Dr. W. B. Davidson for the Ministry of Munitions. At that time there was an urgent demand for toluol, but practically none for benzol. In view of this fact, and of the necessity then existing for maintaining the illuminating power of the gas, benzolised creosote was used as wash-oil, with the object of absorbing toluol from the gas and at the same time adding benzene to it. The gas was accordingly washed, in tower scrubbers, with a mixture of creosote and 5 per cent. of benzene. Nearly 80 per cent. of the toluol in the



gas was recovered in the subsequent distillation, which was carried out in a plant of the usual debenzolising type. The process was applied to some 800 tons of coal per diem, but, although very successful, it had to be abandoned at an early date owing to the demand for benzol as well as toluol.

### Steam Distillation

The vapour pressure of a liquid increases with rise of temperature. When this pressure becomes equal to that of the atmosphere the liquid rapidly changes into the vapour phase, and is said to boil. Suppose a mixture of carbon disulphide (boiling point  $46^{\circ}$  C.) and benzene (boiling point  $80^{\circ}$  C.) to be heated. When the mixture reaches  $46^{\circ}$  C. the vapour pressure of the carbon disulphide is 760 mm. and it therefore boils. The temperature of the mixture will remain at  $46^{\circ}$  C. until most of the carbon disulphide has boiled off, and as the vapour pressure of benzene at that temperature is only about 245 mm. very little of the latter vapour is evolved. After all the disulphide has been vaporised, however, the temperature rises to  $80^{\circ}$  C. when the benzene in turn boils.

In practice the process is not quite as simple and straightforward as the foregoing, but this will serve to indicate the broad principles of fractionation. In debenzolising wash-oil we require to distil off, in addition to benzol and toluol, other substances of higher boiling points, such as xylol and naphthalene. At the same time it is desirable to avoid excessively high temperatures for economic and other reasons, and steam distillation is therefore resorted to. In debenzolising, which is a continuous process in most cases, we have a constant supply of benzolised oil, and, therefore, of crude benzol, passing through a heating system whereby its temperature is raised to about  $120^{\circ}$  C. In this portion of the plant most of the benzol, some of the toluol and a small proportion of the solvent naphtha are eliminated. The hot oil thereupon passes through some form of still in contact with a current of steam; the heavier vapours are given off and pass away with the steam.

The explanation of this is connected with the vapour pressure of mixed liquids. The total vapour pressure of two non-mixing liquids has been stated to be equal to the sum of their separate vapour pressures at the same temperature. When, therefore, xylene and steam are heated together, the mixture boils when its *total vapour pressure* becomes equal to that of the atmosphere. In other words a mixture of xylene (boiling point  $140^{\circ}$  C.) and water will actually pass over to the condenser at a temperature lower than the boiling point of either constituent when heated alone, *i.e.*, below  $100^{\circ}$  C. This, then, is the explanation of steam distillation, and it may be further illustrated by the following example, which also indicates what is, perhaps, the simplest

method of finding the boiling point of such a mixture. Taking benzene and water, we find, by rough addition of their vapour pressures at a few temperatures, that their boiling point when mixed lies between  $64^{\circ}$  and  $72^{\circ}$  C. Their vapour pressures at various intermediate temperatures are tabulated and added thus :

TABLE 13.—VAPOUR PRESSURES OF BENZENE AND WATER.

Temperature, ° C.	64°	66°	68°	70°	72°
Vapour pressure of benzene	441	472	505	544	580
„ „ water	179	196	214	234	255
Total vapour pressure	620	668	719	778	835

These total vapour pressures are plotted against the respective temperatures, and the boiling point of the mixture is found where the curve cuts the 760 mm. line, in this case  $69.4^{\circ}$  C. The vapour pressures at this temperature are 533 mm. in the case of benzene, and 227 mm. for water. Similarly, the boiling point of a mixture of meta-xylene and water is  $93.1^{\circ}$  C. Reverting to the case of benzene and water, we may now find the proportions in which these constituents will distil. On boiling at  $69.4^{\circ}$  C. we have a mixture of the vapours of benzene and water, in which the partial pressures are 533 mm. and 227 mm. respectively. The amount of each vapour present is, by the law of partial pressures,

TABLE 14.—STEAM DISTILLATION OF ORGANIC COMPOUNDS.

MIXTURE OF WATER AND :	Boiling point of mixture. ° C.	Vapour pressures at boiling point. • Mm.		Composition of vapour. Percen- tage by volume.		Composition of dis- tillate. Percentage by volume.	
		$C_nH_m$ .	Water.	$C_nH_m$ .	Water.	$C_nH_m$ .	Water.
Carbon disul- phide .	43.5	693	67	91.2	8.8	97.2	2.8
Benzene .	69.4	533	227	70.1	29.9	92.0	8.0
Toluene .	84.2	338	422	44.5	55.5	82.5	17.5
Ortho-xylene	93.5	160	600	21.1	78.9	64.5	35.5
Meta-xylene .	93.1	172	588	22.6	77.4	66.4	33.6
Para-xylene	92.8	177	583	23.3	76.7	67.3	32.7
Naphthalene.	99.4	18	742	2.4	97.6	12.7 *	87.3

\* Measured as liquid.

proportional to this. Multiplication by the gaseous volume of 1 gallon of each liquid—or multiplication by the vapour density and division by the specific gravity of the liquid—will then give the proportion of each liquid by volume in the distillate. In this way the values in *Table 14* have been calculated.

Creosote being a variable mixture, its vapour pressure is not known, but it is probable that a mixture of creosote vapour and steam would give, at a boiling point of practically  $100^{\circ}\text{C.}$ , a distillate containing only 1—2 per cent. of creosote. It is due to this steam distillation effect that we can eliminate naphthalene from wash-oil without raising it above a temperature of, say,  $120^{\circ}\text{C.}$ ; for when the quantity of steam admitted to the still is greater than that required to distil over all the crude benzol in the oil (as found from the above table), the excess of steam serves to bring over compounds of progressively higher boiling point. Thickening of wash-oil is also due mainly to this cause.

The operation of debenzolising wash-oil is therefore a complicated matter, and one which cannot be controlled by any simple consideration of boiling points. Advantage is taken in practice of the constancy of the conditions; and since, for any particular plant, the supply and saturation of the benzolised oil are practically invariable, it is a fairly simple matter to find the conditions under which the plant will give the best results, and to maintain these conditions.

### Effect of Incomplete Stripping of the Oil

The effects of incompletely debenzolising the oil, whereby partially benzolised oil is returned to the scrubbers, are very similar to the results of over-saturation during the washing of the gas. Failure to strip the whole of the crude benzols from the oil may be due to one or more of four main causes:—

- (i.) Too low a temperature of oil entering the still.
- (ii.) Insufficient open steam.
- (iii.) Low time-contact in the still.
- (iv.) Drastic fractionation.

A study of vapour pressures and steam distillation will show that the benzol will be the fraction most readily driven off in the still, as well as the one having the least tendency to condense in whatever fractionating column may be used (excluding, of course, the light “pre-benzols”). Thus the efficiency of the still is much higher for benzol than for toluol, and still more so than for xylol. The “benzol” left in the oil is, therefore, very much richer in the heavier fractions than is the crude spirit produced, and, in fact, under such conditions the latter is always of a high quality, containing very little—if any—naphthalene. When this oil is returned to the scrubbers it will evidently be less efficient than a well-stripped oil for reasons given when considering the effects of over-saturation. In practice, however, the plant is worked

at a sufficiently high temperature and with enough open steam to drive over all the benzols, together with most of the naphthalene and some of the lighter fractions of the creosote.

### Fractionation

Fractional distillation is more in evidence during the rectification process, but will be briefly mentioned here since it also occurs, to a certain extent, in most crude benzol plants. Some of these plants, in fact, have columns added for this purpose, whilst in others the action takes place in the upper portion of the still. Fractionation entails the condensation of the heavier portions of the vapours and their return to the still (or removal for the recovery of naphthalene), after they have washed the vapours and steam ascending the column. A fractionating column is, therefore, a combination of reflux condenser and scrubber. The advisability of drastic fractionation on a debenzolising plant is a matter of some doubt, except in so far as the addition of a column for this purpose gives greater control over the quality of the product, and adds in a small degree to the useful life of the wash-oil. When the condensate, however, is taken from the column and allowed to cool, instead of refluxing into the body of the still, such an arrangement is an undoubted advantage. Naphthalene may then be separated from the cooled oil, the liquid portion of which is returned into circulation and so delays the rejection of the wash-oil, through thickening. This subject will be more fully discussed in Chapter VII.

### Thickening of Wash-oil

After a certain time in use wash-oil becomes "fatigued," and its viscosity increases, whilst at the same time, its absorbent powers are diminished to such an extent, that it must be rejected and replaced by new oil. This thickening is generally ascribed to the removal, by repeated steam distillation, of the lighter fractions; but, whilst these constituents undoubtedly contribute in no small degree to the fluidity of the oil, their removal cannot entirely account for the amount of thickening often experienced. When crude gas is oil-washed, tar fog often finds its way into the wash-oil, and causes an increase in its "free-carbon" content and viscosity; whilst on direct-fired plants there is frequently a certain amount of cracking, due to local over-heating, which also results in free carbon and thicker oil. The remedy in each of these cases is obvious. It is possible, however, that a certain amount of resinification also takes place in consequence of the repeated heating and cooling of the oil. Several resin-forming compounds occur in crude benzol which, under the action of heat, are readily oxidised into high-boiling resins. Among such compounds are dicyclopentadiene ( $C_{10}H_{12}$ ) and coumarone ( $C_8H_6O$ ).

### Rectification

Little need be said at this point about the theoretical principles underlying rectification, except to point out that the subsequent distillations of the various benzol fractions are almost invariably intermittent processes. Thus, in the preliminary distillation of crude benzol, the liquid is subjected to the action of heat alone—with, of course, a certain amount of fractionation—until all the benzol and toluol has been driven off. Open steam is then, and only then, introduced. In some cases the later stages of the distillations are completed under a slight vacuum.

## CHAPTER III

### THE EXTRACTION OF BENZOL FROM GAS

THE extraction of benzol vapours from gas mainly depends upon the type of washer or scrubber used, the quality and conditions of use of the wash-oil, and upon the combination of these two factors in practice to give the best and most economical result. The form of apparatus in use for this purpose is the same as that used for ammonia extraction, and most forms of the latter may be applied, more or less successfully, to benzol recovery. We have seen that the efficiency of washing is dependent upon several conditions, the chief of which are :—

- (i.) Intimacy of contact between oil and gas.
- (ii.) Time-contact of gas with absorbent.
- (iii.) Extent to which the operation approaches counter-current conditions.

#### Types of Washers and Scrubbers

Before considering the washing process it is as well to examine the usual types of washers from this standpoint. Reference may be made for further details to Alwyne Meade's valuable book.\*

##### *The Livesey Washer*

The Livesey washer may be said at once to be an undesirable form of apparatus for this purpose. It is briefly considered here since, owing to the exigencies of war-time, this washer is in use as a benzol extractor on many gasworks. In addition to giving a great deal of back pressure this washer fails to fulfil any of the above conditions. Intimacy of contact is difficult, if not impossible, of attainment, owing to the large bulk of oil in the body of the apparatus. This defect should be avoided as far as possible by filling the Livesey with bricks or other material to within 2 or 3 inches of the bottom of the bubbling troughs, thus increasing the rate of oil-flow through the washer to a maximum. Since the apparatus comprises only a single chamber, contra-current working is impossible, and in order to reach any appreciable rate of recovery the amount of wash-oil used must be considerably in excess of the theoretical. Time-contact is obviously low and depends upon depth of seal and amount of frothing on the surface

\* "Modern Gasworks Practice," by Alwyne Meade. Benn Bros.

of the oil, which, in turn, vary with the permissible back pressure and the viscosity of the oil.

The original type of Livesey washer contained double troughs, as at *a* (FIG. 6), the lower one being perforated and the upper one serving as a duct to lead the gas to the outlet chamber. Thus the gas enters the body of the washer, depresses the oil level, and bubbles through two sets of perforations, and so, in a finely divided state, through the oil. In some forms of the apparatus now on the market the troughs are single and are perforated near their lower edges only. In such a case (*b*, FIG. 6) the froth is broken up almost as soon as it is formed in the trough, and very low time-contact results. In some instances in the author's experience the efficiency of such a washer has been considerably increased by reversing the flow of gas through the perforations

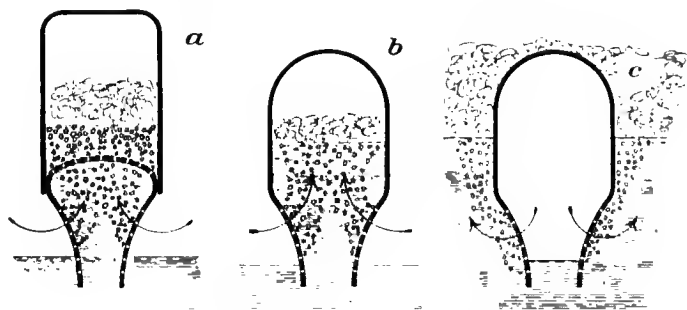


FIG. 6.—TROUGHS OF LIVESEY WASHERS.

as at *c* (FIG. 6). The improvement was due, of course, to the formation of a greater depth of froth on the surface of the oil.

When two or more Livesey washers are in use, they should be worked in series whenever the works' seals will withstand the extra pressure, and in such a case the washers should be erected at different levels, so that the contra-gas flow of the oil may be effected by gravity.

### *Tower Scrubbers*

Tower scrubbers are commonly used for oil-washing on by-product coke-oven plants. Such scrubbers, working under the best conditions, are undoubtedly very satisfactory; and if they are of fair height compared with diameter give a good practical approximation to counter-current flow. As regards only the washing process, the efficiency of a tower scrubber increases with its height, but there are other considerations such as cost and difficulty of erection, cost of pumping, etc., which limit the ratio of height to diameter, the usual value of which is 4 or 5. For complete recovery of benzol in a tower scrubber, the capacity

of the latter should be from 3 to 5 cubic feet per 1,000 cubic feet of gas per (maximum) day, the figure varying with the type of packing in use, and, of course, with the benzol content of the gas. Thus, under average conditions, a works carbonising 100 tons of coal per diem in mid-winter would require scrubber capacity of about 4,500—4,800 cubic feet. This is furnished by a tower 50 feet high by 11 feet diameter. The efficiency may also be

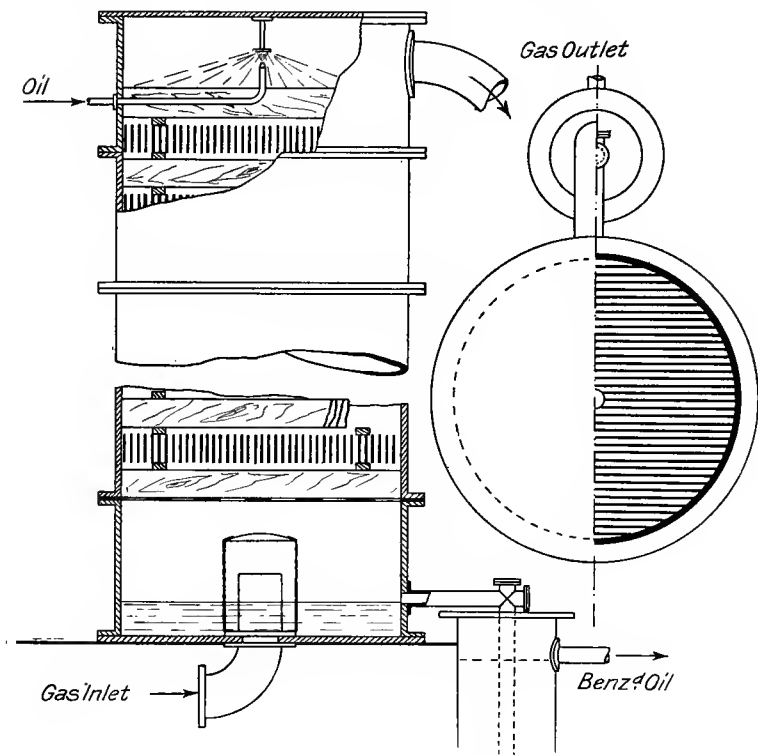


FIG. 7.—TOWER SCRUBBER WITH BOARD FILLING.

increased slightly by dividing the requisite scrubbing volume into two towers, but the advantage of such an arrangement is neutralised by the necessity of providing an extra tank and pump, and by the cost of recirculating oil over the rich-gas tower. A single tower is the better arrangement for works of medium size.

Tower scrubbers are filled with coke, brushwood, earthenware balls, drain-pipes, boards on edge, or Raschig rings, boards being the usual material as well as probably the most satisfactory,



when considered from all points of view. Raschig rings, which will be mentioned later, of 1—3-inch diameter and the same length, are mechanically the most efficient filling, but their high first cost and the difficulty of their removal for cleaning prohibit their use in any but the smallest towers. Board filling is expensive, but on the other hand, it is easily removed, has a long life and gives a good scrubbing surface, both in character and area, per cubic foot of space occupied. The boards are usually of  $6 \times \frac{1}{2}$ -inch section and are built into trays of suitable size. The space between the boards should be about  $\frac{3}{4}$  inch, whilst  $2 \times 2$ -inch battens serve to separate the trays. A tower scrubber packed in this manner is shown in FIG. 7.

The comparative utility of the various fillings is given in Table 15. From this table it will be seen that coke, although

TABLE 15.—FILLINGS FOR TOWER SCRUBBERS.

MATERIAL.	Size.	Square foot surface per cubic foot capacity.	Percentage of sectional area occupied.
Coke . . .	—	8—9	About 50
Drain-pipes . .	3 inches dia.	17—18	—
Boards . . .	$\frac{1}{4}$ inch thick, $\frac{3}{4}$ inch apart.	30	25
Raschig rings .	$1 \times 1$ inch	50	About 18—20

the cheapest filling, is relatively very wasteful of scrubber space, whilst it also throws much more back pressure than other packings as indicated by column 4. This material, and also brushwood, are very difficult to remove for cleaning, and, moreover, have a strong tendency to "rat-holing," *i.e.*, uneven distribution of gas and oil flow. In fact, this question of distribution, upon which depends intimacy of contact, is one of the most serious disadvantages of the tower scrubber. It is essential that the oil be sprayed evenly over the packing, and for this reason a scrubber should always be of circular section in preference to square or rectangular. The introduction of the oil may be effected by perforated pipes, corrugated and perforated diaphragms, or by a "Barker's mill," although the well-known Gurney's jet is probably the best device for this purpose. A single centrally placed jet is sufficient for a small scrubber, but one of, say, 15-foot diameter should have four such distributors, spaced evenly around the outlet pipe.

#### *Rotary (Horizontal) Washer-scrubbers*

There are many forms of these machines on the market, varying in details of design and in the construction of the rotatory scrubbing members. All are excellent washers for benzol

extraction. A typical one, Messrs. Kirkham, Hulett and Chandler's "Standard" machine, is shown in FIG. 8, for the block of which the author is indebted to Alwyne Meade.

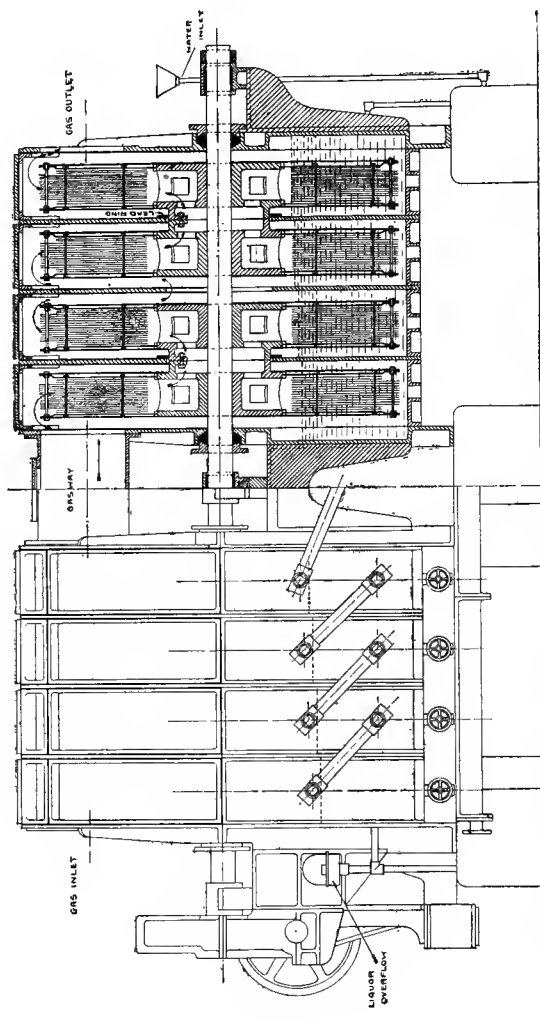


FIG. 8.—KIRKHAM, HULETT AND CHANDLER'S "STANDARD" WASHER-SCRUBBER.

In this machine the washing takes place progressively in 4, 6, 8, or 12 bays, the flow being counter-current and the lower portion of each bay being filled with oil. A circular "disc" of

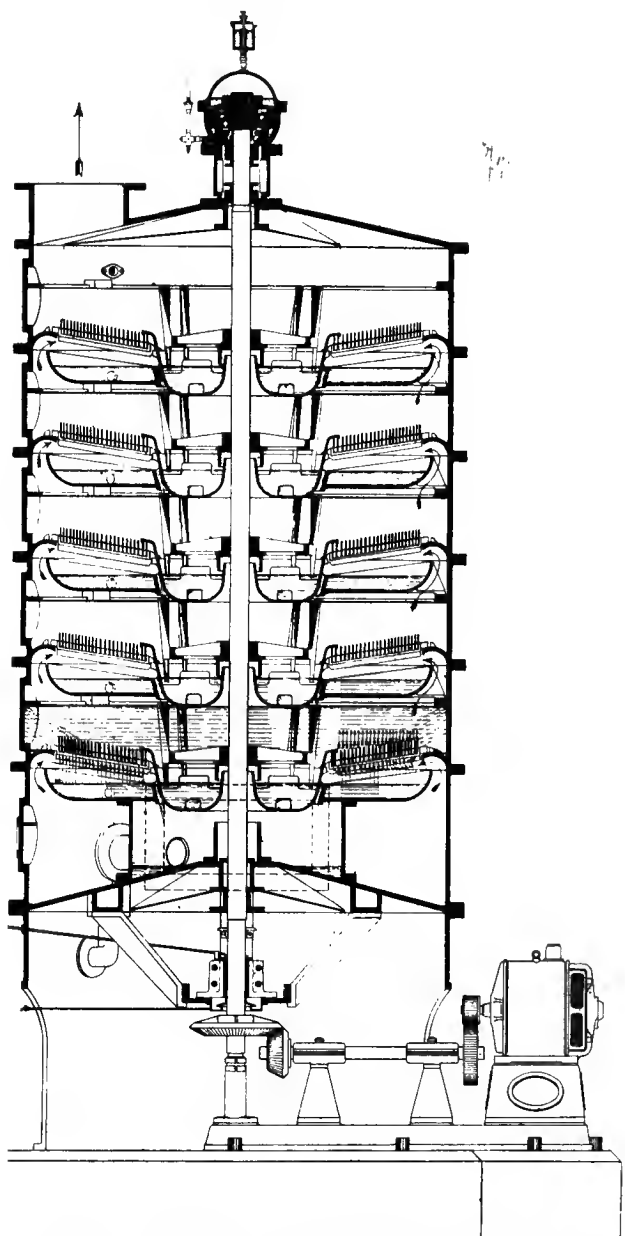


FIG. 9.—HOLMES' VERTICAL CENTRIFUGAL WASHER.

sector-shaped bundles rotates in each bay, passing through, and being moistened by, the oil once in every revolution. The bundles leave the oil and, whilst wet, are presented to the gas passing over them. In the machine illustrated the bundles may be composed of wooden laths, sheet iron or of plates of corrugated iron; the last-named presents a large wetted surface to the gas and holds the oil well. In Messrs. Clapham Bros.' "Eclipse" washer the bundles are hollow and filled with perforated wooden balls, whilst Messrs. W. C. Holmes, Ltd., use brushes which rub on the division plates, thus preventing short-circuiting. The bristles in these brushes were formerly fixed with molten pitch which dissolves in creosote and so loosens the bristles. This difficulty is overcome by the use of wooden pegs in place of the pitch. All these rotary machines make excellent benzol washers, their chief advantage being the progressive counter-current nature of their action.

### *Centrifugal Washers*

Centrifugal (vertical) washers have during the last few years proved their worth, not only as ammonia and cyanogen extractors, but also as absorbers of benzol. In these appliances the washing is performed by means of a fine spray of oil, in a series of super-imposed trays or sections, through which the gas ascends in turn,

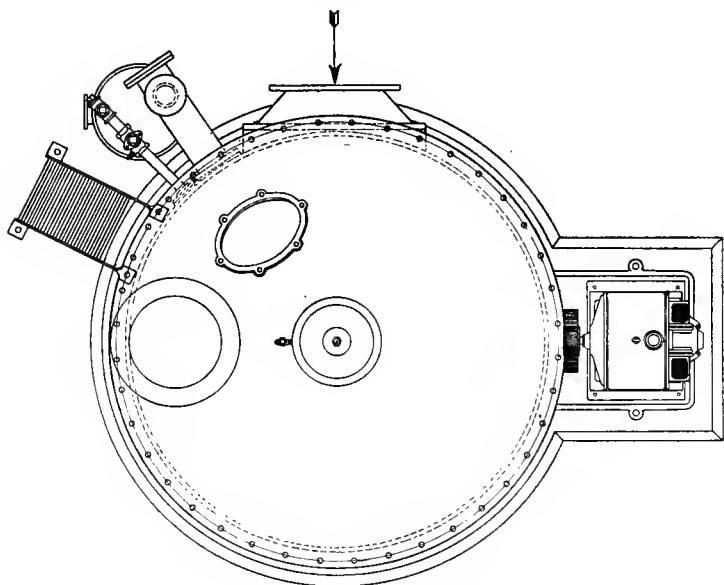


FIG. 9A —PLAN OF FIG. 9.

and in which very intimate contact between gas and oil is attained. Each tray contains a quantity of oil, and the spray is produced by a device—usually a reversed Barker's mill—mounted on a central vertical shaft and revolving at 120 or 150 revolutions per minute. The oil overflows from tray to tray in a direction opposed to that of the gas, and, by the use of eight or more sections, a high degree of saturation may result. These washers offer several advantages, among which we may notice the small ground space occupied, the counter-current flow and intimacy of contact, whilst neither the first cost nor power consumption are excessive. The first successful centrifugal washer was that of Dr. Feld, and several types are now on the market. One which has proved very suitable for oil washing is that patented by the author's former chief, Dr. W. B. Davidson, and constructed by Messrs. W. C. Holmes, Ltd. This machine is shown in FIGS. 9 and 9A, from which it will be seen that the gas passes in an upward direction through a number of spraying chambers or trays. A feature of the washer is the suspension of the vertical shaft carrying the moving parts, from an adjustable and well-lubricated ball-bearing at the top, instead of its being supported by the usual collar bearing at the top and footstep at the base. Each tray contains an annular oil reservoir into which dip scoops which revolve at 120—150 r.p.m., and serve to pick up the oil. The upper extremity of each scoop forms a distributor, being slotted horizontally, and throws off the liquid in the form of a very fine spray. The path of the gas is so regulated by suitable guides, and by a gallery formed of concentric rings of flat iron, as to be brought into intimate contact with the spray filling the chamber. Suitable sealed overflows are provided for the passage of the oil from tray to tray, and the shaft is driven by bevel gearing beneath the machine. This apparatus forms a most efficient benzol extractor, its chief advantages being :—

- (i.) Counter-current nature of action.
- (ii.) Low back pressure thrown.
- (iii.) Intimacy of contact between gas and oil.
- (iv.) Low power consumption.
- (v.) Small ground space occupied.
- (vi.) Accessibility of all parts, and little liability to choking of distributors.

#### *" Cascade " Washer*

When it is desired to extract only a portion of the benzol from the gas, as is the case at present in most gasworks, it is advisable to work at a saturation no higher than normal. For reasons to be explained later, it is the better plan to by-pass a portion of the gas from the scrubber, rather than to effect a lower rate of recovery by the use of a reduced quantity of wash-oil per ton of coal. When a new scrubber is to be purchased for oil washing under

these conditions, it is obviously cheaper and more satisfactory to erect a simple form of apparatus of comparatively low efficiency. Such is Wilton's "Cascade" washer as made by the Chemical Engineering Co. This is shown in FIG. 10, and is in the form of a tower consisting of a number of cast-iron trays. The smaller segment of the base of each tray is cut away, and along the chord so formed is placed a weir (W, FIG. 10), having a serrated

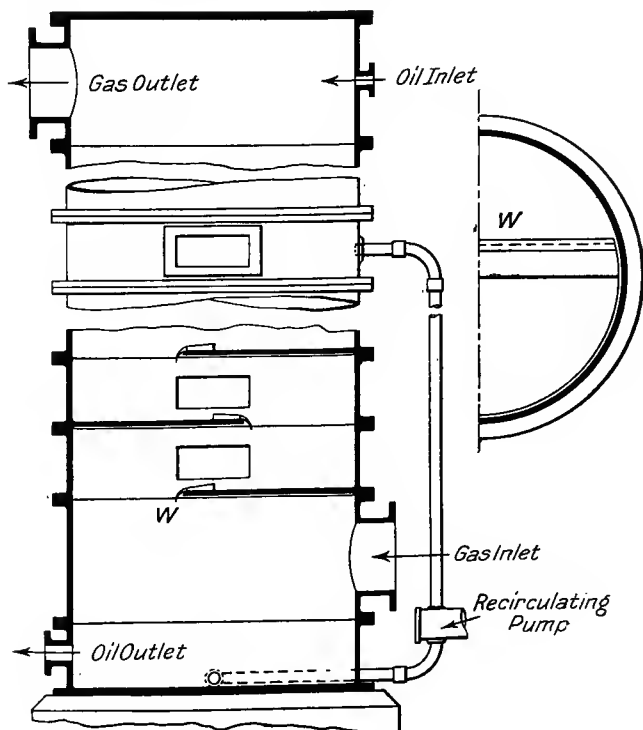


FIG. 10.—WILTON'S "CASCADE" WASHER.  
(Chemical Engineering Co.)

edge. The trays are arranged with weirs alternately left and right, and oil is admitted to the top chamber. The result is a cascade of oil in each tray. The gas enters the bottom chamber and zig-zags through these cascades in turn, and over the surface of the oil remaining behind each weir, so that the arrangement gives a fair approximation to counter-current flow.

The efficiency of this washer is admittedly low, owing to little time-contact and other causes, and a low saturation is obtained with only one passage of oil through it. To reach a higher

saturation, a small recirculating pump draws oil continuously from the reservoir at the base of the tower, and returns it to a tray about halfway up the washer. Fresh debenzolised oil is fed to the top tray, and in this way partly saturated oil is recirculated over the lower half of the washer. The result is a higher saturation of the benzolised oil passing away to storage. The chief advantages of this form of apparatus are its comparatively low cost and the very small amount of pressure it absorbs.

Disadvantages are the low efficiency (though this was known when it was designed) and the larger quantity of wash-oil to be debenzolised in consequence. The latter, however, as will be seen later, is a distinct advantage from the point of view of naphthalene recovery.

### Choice of Scrubbing Plant

The type of washer to be installed depends upon the foregoing considerations, as well as upon first cost, maintenance, and the extent to which the gas is to be denuded of benzol. The " Cascade " washer is only intended for partial stripping ; the Livesey cannot be said to be desirable for oil washing, though its cost and upkeep are low. For complete stripping we must have either a large tower scrubber or a mechanical washer. A rotary machine 8 feet in diameter and comprising ten bays will easily strip the gas from 150—170 tons of coal per diem, and the same effect will be produced by a centrifugal of eight bays, 6 feet 6 inches in diameter. A mechanical washer is, therefore, much smaller and entails less expense in foundations than a tower. The first cost of a tower packed with boards is some 20 per cent. higher than that of a rotary washer or centrifugal, and the power consumption of the latter types is comparatively small. Alwyne Meade (*Modern Gasworks Practice*, 1st Ed., p. 347) gives the following figures :—

TABLE 16.—POWER REQUIRED TO DRIVE MECHANICAL WASHERS.

CAPACITY OF WASHER.	HORIZONTAL.	VERTICAL.
500,000 cubic feet per diem	3 H.P.	4 H.P.
1,000,000     "     "	4     "	5     "
2,000,000     "     "	5     "	7     "
3,000,000     "     "	6     "	10     "

The power consumption is, therefore, comparatively small, and when one considers the higher efficiency of the mechanical washer and the smaller steam consumption for pumping, together with the difficulty and expense of periodically cleaning a tower scrubber, the advantage clearly lies with the former type

### Position of Scrubbers

Scrubbing should be performed at a point where the gas is as cool and as completely purified as possible, in most gasworks at the outlet of the oxide purifiers. The necessity for cool gas has already been emphasised ; and if crude gas be washed there will be a greater proportion of impurities in the benzol. There is also a tendency for the hydrogen sulphide and traces of ammonia present in crude gas to cause corrosion of the debenzolising plant, whilst the presence of even a trace of tar fog is a serious disadvantage. Many gasworks, however, are oil washing before the purifiers, chiefly because they were compelled to do so by the shortage of materials when meeting the war-time requirements of the Ministry of Munitions. The only case in which

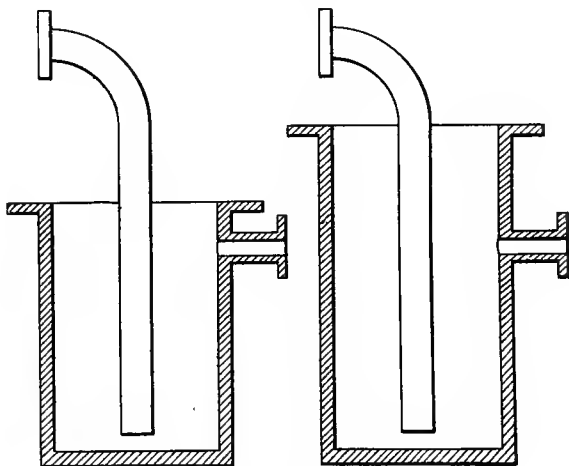


FIG. 11.—SEAL POTS ON SCRUBBERS.

oil washing should be commenced before the purifiers is one where the gas, through lack of purifier space or other cause, is heated considerably by the purification process.

The size of gas connections to scrubbers will be predetermined by the size of the works ; as regards oil connections, nothing less than 2-inch pipe should be used on any but the smallest works. Whilst a smaller pipe may deal easily with fresh creosote, it may be found far too small when the viscosity of the latter increases. For the same reason there should be as much fall as possible between the seal pot of the scrubber and the benzolised oil tank ; whilst on this account, and also because of a marked tendency to frothing on the part of new oil leaving the scrubber, such seal pots should be designed with ample depth above the oil outlet. This is indicated in FIG. 11.



Joints on scrubbers, and, in fact, on any work coming into contact with gas, creosote or benzol, should have special attention. Faced joints must be insisted upon throughout, and undoubtedly the best form of this is an annular facing strip surrounded by a good depth of iron borings and sal-ammoniac. The construction of this kind of joint is shown in FIG. 19 on p. 61.

As has been pointed out, the ideal arrangement of scrubbing plant is one which gives truly counter-current flow, with intimate and long contact between cool gas and oil. If two scrubbers or washers are used, they should, therefore, be placed in series wherever the conditions as to back pressure will allow.

### Wash-oil

The question of the quality, character and properties of the absorbing medium is of the utmost importance, and upon these factors to as great an extent as upon any other depends the efficiency of the process. It may be said at the outset that the oil must conform to the following main conditions, in addition to freedom from water :—

- (1) Its specific gravity should be as far removed from 1.0 as possible, consistent with other requirements.
- (2) Its specific heat must be as low as possible.
- (3) The amounts of naphthalene and anthracene must be reduced to as little as possible.
- (4) The viscosity must be low.
- (5) It must not become unduly viscous on distillation.

The importance of these requirements is evident from the following considerations :—

### *Specific Gravity*

If the density of the oil is approximately equal to that of water, much trouble will be caused in the event of any water becoming admixed with it. This is not always avoidable, and as will be seen later it must, if excessive at any rate, be removed by settling and decantation. An oil of specific gravity near 1.0 will require a much longer time for such settling than one of considerably higher (or lower) gravity. For this reason the use of mixtures of creosote and blast furnace or similar light oil is to be condemned. Such an admixture has been advocated on some occasions on account of the consequent reduction in naphthalene content, but the difficulty of separating water may more than counteract any advantage in this respect. But water in oil frequently manifests itself as an emulsion, and there is no doubt that the liability to emulsification increases as the specific gravity of the oil approaches unity.

*Specific Heat*

In the extraction of 1 gallon of crude benzol some 20 or 30 gallons of wash-oil must be heated from atmospheric temperature to about 120° C. and afterwards cooled again, usually by means of water. The quantity of heat to be added and abstracted—as steam and cooling water respectively—evidently varies with the specific heat of the oil, and for economical working this value should therefore be as low as is practicable. In practice, however, it is found that an oil which is satisfactory as to other requirements will usually have a reasonably low specific heat, the value of which for an average creosote is about 0.4.

*Naphthalene and Anthracene Content*

As will be remembered by many readers, oil washing results in a tendency to aggravated naphthalene trouble. An oil-washing plant may be so worked as to act also as a naphthalene extraction plant, and this matter forms the subject of a later chapter. If an oil be used containing in its original condition an excess of naphthalene, this substance cannot be entirely eliminated by one, two, or even three passages through the distillation system. The result is that the gas is washed with an oil in which the naphthalene exerts a considerable vapour pressure.

The same rules as to absorption apply in the case of naphthalene as in that of any other vapour, and it is clear that under these conditions not only will there be no extraction of this troublesome hydrocarbon from the gas, but the quantity in the latter may actually be increased, whilst at the same time its content of so-called “carriers” is reduced. Such conditions make for trouble on the district, and the difficulties do not end there, for an oil rich in naphthalene tends to deposit crystals—in the form of a sludge—on cooling. Thus tanks, connections, pumps, etc., are liable to give trouble through this cause.

During the war the tar distillers found it difficult, owing to the demands made upon them as well as to lack of labour and plant, to allow their creosote a sufficiently long settling period, and wash-oils frequently contained from 15 to 25 per cent. of naphthalene. These abnormal amounts should not, however, be tolerated now, as there is no great difficulty in reducing the figure to 6 or 7 per cent. even without special treatment, such as refrigeration. An oil containing not more than 7 per cent. of naphthalene may be used with a fair degree of safety.

Anthracene does not occur to any material extent in creosote wash-oils, but “green-oil,” for which some workers express a preference, is apt to contain sufficient to cause trouble; the reason being, of course, the comparatively low market value of the product. Anthracene does not give rise to stoppages on the district as far as the writer’s experience goes, but it is very

apt to cause blockages on the plant, *e.g.*, in coolers and pipe connections, on cooling of the oil. A naphthalene stoppage in such a position presents comparatively little difficulty, since it is easily moved by hot oil or steam. Anthracene, however, has a considerably higher melting point and is much more difficult to clear, dismantling of the apparatus being frequently necessary. Green-oil for gas washing should not contain more than about 2 per cent. of this substance.

### Viscosity

This property of the wash-oil is of vital importance, both in the washer or scrubber and also in the debenzolising plant. It has been shown that the effective working of the scrubbing system depends upon distribution of gas and oil, and upon the intimacy of contact between them. In a rotary washer a viscous oil will not distribute itself over the bundles or brushes as well as

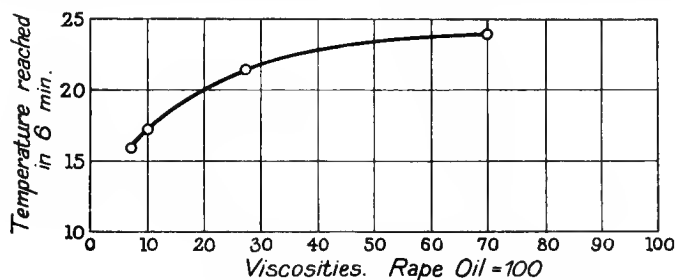


FIG. 12.—EFFECT OF VISCOSITY ON THE COOLING OF CREOSOTE.

one of greater mobility, whilst the poorer distribution over a tower scrubber or centrifugal machine is apparent. On the debenzolising plant, too, the effect of high viscosity is very detrimental. A smaller proportion of the oil comes into contact with the heating elements of the preheater, and inferior distribution is obtained in the trays of the still.

As regards heat exchangers and coolers the effect is more marked, since "core-flow" results from the increased friction between oil and pipe. Both heating and cooling in a benzol plant depend to a great extent upon convection, and the more viscous the oil the less is this effect produced. The viscosity of new creosote is usually about 7 at 60° F. (rape-oil having viscosity 100 at the same temperature), and whilst in use the value should not be allowed to exceed 15—18.

T. F. E. Rhead (*Proc. Junior Gas Assoc.*, 1916—17) describes some experiments to illustrate the effect of viscosity on cooling. The times taken by different creosotes to cool from 120° to 15° C.

under similar conditions were taken, and the results are shown in FIG. 12.

Naphthalene has a very curious effect on the viscosity of oil in which it is dissolved. The addition of naphthalene to creosote actually renders it more fluid within certain limits. Rhead (*loc. cit.*) quotes the case of a creosote of viscosity 10.5 at 15° C. The addition of 10 per cent. naphthalene reduced the viscosity to 9.5 at the same temperature.

The test for viscosity of oil is carried out in the Redwood standard viscometer, and the method is too well known to need description here. It is not always convenient to obtain rapè-oil as a standard, although viscosities are referred to this oil, the viscosity of which is taken as 100 at 15.5° C. It is convenient to remember that the viscosity of water at the same temperature is 5.21. If, as on many gasworks, a Redwood instrument is not available, this test may be performed with sufficient accuracy for works purposes with a pipette. A 100 or 200-c.c. pipette has an additional graduation scratched on the stem an inch or two above the jet. It is filled with water to a point above the top mark and the water is then allowed to run out. By means of a stop-watch, a measurement is made of the time taken by the water to run out from the higher graduation to the lower. This procedure is repeated with the sample of oil under test, the viscosities of the liquids being approximately proportional to the time taken.

Thus the viscosity of creosote on the rape-oil scale is

$$5.21 \times \frac{T_c}{T_w}$$

where  $T_c$ ,  $T_w$  are the numbers of seconds taken by the creosote and water respectively to traverse the distance between the graduations.

## Varieties of Wash-oil

### *Creosote Oil*

This oil is undoubtedly the most satisfactory providing its naphthalene content is sufficiently low. The specification of the Department of Explosives Supply for this oil is as follows :—

Specific gravity	. 1.020—1.030 at 60° F.
Tar acids	. Immaterial.
Naphthalene.	. Should deposit none on cooling to 55° F.
Boiling point	. Should not boil below 200° C.
Distillation	. Not less than 70 per cent., nor more than 90 per cent. at 300° C.

The viscosity of such an oil is usually about 7, and a wash-oil conforming to this specification may be relied upon to give good results. This grade of creosote usually contains tar acids to the

extent of 8—9 per cent., but these are rather an advantage than otherwise since naphthalene is much more soluble in these acids than in the remainder of the oil. Their effect in this direction is not of long duration since they are steam-distilled into the crude benzol. Water is slightly soluble in creosote, but should not be present to a greater extent than 1 or  $1\frac{1}{2}$  per cent. in a well-settled oil.

### *Green-oil*

Many workers prefer a heavier wash-oil than creosote, and such a material is found in "green-oil" or "strained-oil." This results from the coal-tar fraction coming over after the creosote and extending to the end of the operation, *i.e.*, to pitch. This fraction, known as anthracene-oil, is allowed to cool and settle any solid matter, after which it is strained. By this means, some 6 to 10 per cent. of solid crude anthracene is recovered, containing about 30 per cent. of the pure hydrocarbon. The strained-oil varies in specific gravity from 1.08 to 1.1; it commences to distil at about 220° C., giving 25—30 per cent. at 300° C. and 75—80 per cent. at 370° C.

There are certainly a number of advantages to be derived from the use of this oil instead of creosote, among which may be noticed its comparative freedom from naphthalene, its higher specific gravity, and the fact that its higher boiling range makes it possible to produce a better quality of crude benzol, the wash-oil at the same time having a somewhat longer life in consequence. These advantages, however, are to some extent counterbalanced by certain drawbacks, the chief of which are the greater viscosity of the oil and the liability to anthracene blockages on the plant, particularly in the oil coolers.

The viscosity of an average green-oil when fresh is about 10, as compared with 7 for creosote. Anthracene stoppages are difficult to clear without dismantling the apparatus, owing to the fact that anthracene, which melts at 216° C. and is not very soluble in the oil, cannot readily be moved by steaming. Green-oil for gas washing should not contain more than about 2 per cent. of anthracene.

### *Blast-furnace Creosote*

This substance is frequently recommended for gas washing, especially where naphthalene troubles are acute. It results from the washing and cooling of blast-furnace gas, and owing to the low-temperature distillation of the coal in the upper portion of the furnace, is of a paraffinoid nature. The chief attraction presented by this oil is the fact that, for the same reason, it contains no naphthalene. Its tar-acid content is high, often from 20 to 25 per cent., and its specific gravity about 0.95. The specific heat of this oil is from 0.42 to 0.44 and, with a drop point of about 220° C., it gives on distillation about 50 per cent. at

275° C. and 70—75 per cent. at 300° C. As regards boiling point, therefore, it corresponds closely with a moderately heavy creosote.

The absorptive powers of blast-furnace oil appear to be satisfactory, but there is always a risk of obtaining a crude benzol contaminated with paraffins, owing not only to direct distillation with steam, but also apparently to a certain amount of polymerisation in the still. Paraffins are particularly in evidence in benzol distilled from Scotch blast-furnace oils, in consequence of the use of splint coal in the furnaces.

#### *Straw-oil*

The oil commonly employed for gas-washing in the United States is petroleum straw-oil, a pale yellow fraction obtained from crude petroleum immediately after the gas-oil cut. This forms a very good absorbent, although a paraffin; but the advantages which it offers for the purpose are by no means sufficient to warrant its adoption in this country. One of the chief is its property of remaining fluid at low temperatures, and it is readily so at 4° C. The specific gravity of the oil is usually somewhat less than 0.88, and an average distillation test gives: Drop point 240° C., 90 per cent. between 250° and 350° C.

Benzol recovery appears to be carried out at a higher washing temperature in the United States than is usual in this country, and the degree of saturation of the oil is therefore less, 2—3 per cent. being frequently mentioned. Owing to the reduced proportion of open steam required, it is probable the paraffinoid character of the oil presents no serious difficulty.

#### *Gas-oil*

Ordinary gas-oil furnishes a very satisfactory absorbent, and, in addition to freedom from naphthalene and high fluidity, presents similar advantages to straw-oil. It contains, however, a larger percentage of low-boiling paraffins than the latter oil, and these are removed to a considerable extent by steam distillation at 120° C. Before using this oil for benzol recovery it must therefore be passed through the debenzolising plant at as high a temperature as possible and with plenty of open steam. The distillate may be vaporised into the gas after the benzol washers, or used as a naphthalene solvent. A gas-oil thus prepared will give about 16 per cent. between 280° and 300° C. The original gas-oil has a specific gravity, about 0.86, drop point 190° C., and gives about 5 per cent. of distillate at 250° C.

### **Absorption of Sulphur by Paraffins**

A serious disadvantage of these paraffinoid oils, which does not appear to be shared by coal-tar distillates, is the property of absorbing hydrogen sulphide from the gas. When purified gas

is scrubbed, the effect is perhaps negligible, but in view of the number of cases in which benzol is recovered from crude gas this reaction is of interest. The hydrogen sulphide apparently combines with certain constituents of the oil to form complex sulphur compounds—probably mercaptans. These are decomposed at about  $140^{\circ}$  C., and on distillation in the laboratory large volumes of hydrogen sulphide are evolved at about that temperature. Serious corrosion of preheaters has resulted in some cases where crude gas was washed with paraffinic oil, and whilst the author has had very little opportunity of making a thorough investigation he has been led to attribute the corrosion to this effect. It should, however, be pointed out that ammonia appears to be necessary for this reaction to proceed. In each case a trace of ammonia was present, whilst the washing of ammonia-free gas with similar oil has often continued without trouble.

TABLE 17.—PROPERTIES OF VARIOUS WASH-OILS.

DETAILS.	CREOSOTE.	GREEN-OIL.	BLAST FURNACE CREOSOTE.	PETROLEUM STRAW-OIL.	DISTILLED GAS-OIL.
Specific gravity at $60^{\circ}$ F.	1.025	1.095	0.945	0.875	0.860
Approximate viscosity.	7	10	7	5	4
Distillation test :—					
Drop point, $^{\circ}$ C.	200	250	228	250	240
Per cent. at $220^{\circ}$ C.	16	—	—	—	—
„ $250^{\circ}$ C.	44	—	16	—	2
„ $300^{\circ}$ C.	82	28	73	45	18
„ $350^{\circ}$ C.	—	62	—	90	—

These various oils are compared in *Table 17*. It may be concluded that whilst creosote containing 7 per cent. or less of naphthalene is probably the most suitable absorbent, other oils are readily obtainable which offer advantages not possessed by it. In order to attain certain of these advantages, mixtures of tar oils and paraffinoid oils have sometimes been used. This should never be done, since the gravity of the mixture then approaches 1.0, with a resulting tendency to emulsification and difficulty in separating water.

### The Scrubbing Process

The degree of saturation theoretically obtainable has been discussed in Chapter II., but it must be pointed out that the figures there given refer to benzene only, and by the theory of partial pressures are independent of the toluene and other constituents absorbed. In this chapter, the expression “degree of

saturation " will refer to the percentage of crude benzol of, say, 65 per cent. strength dissolved in the oil. This figure varies in practice from 3 to 6 per cent., and depends upon the benzol content of the gas, the efficiency of the scrubbing plant, and the temperature and other conditions under which the operation

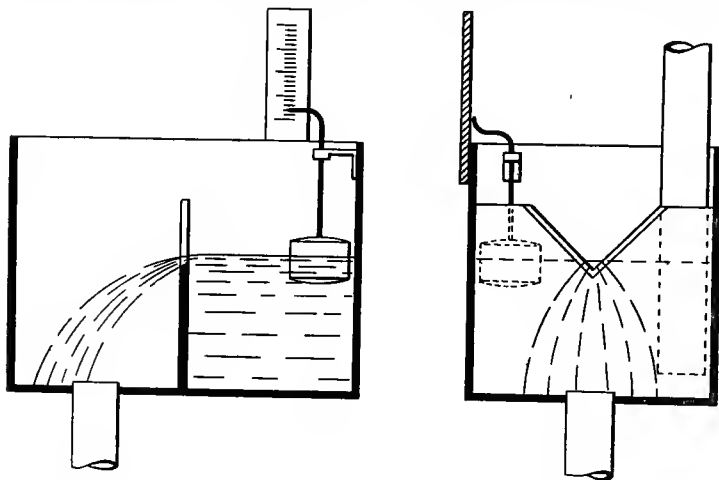


FIG. 13.—MEASUREMENT OF OIL-FLOW BY WEIR.

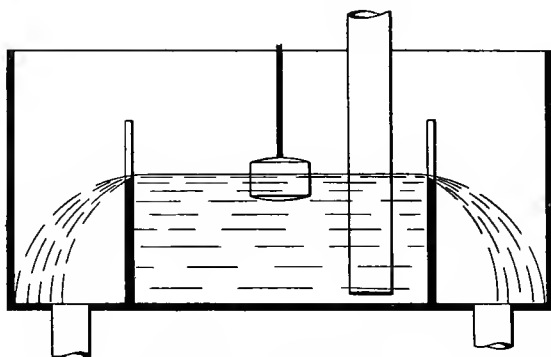


FIG. 14.—USE OF WEIRS TO DISTRIBUTE OIL TO SCRUBBERS.

proceeds, also upon the quantity of oil used per unit volume of gas. The last is usually taken as 12,000 cubic feet or the production from 1 ton of coal. The quantity of oil used varies from 50 to 100 gallons per ton of coal, so that clearly the recovery of benzol cannot be stated in terms of saturation only. Moreover, the whole of the benzol content of saturated oil is not extracted on the debenzolising plant. The make of gas on the average



gasworks and coke-oven plant varies from half-hour to half-hour, but it is not usual to vary the oil flow accordingly. There is usually sufficient oil in the scrubbing plant (especially if this be a rotary washer) to make up for such variations and the question is not important on gasworks where the gas, which is never completely stripped, is subsequently mixed in the holders. With efficient scrubbers which will give a saturation of 5 per cent., a good recovery may be obtained by the use of 60 gallons of wash-oil per 12,000 cubic feet. This corresponds to an extraction of 3 gallons of crude benzol per ton of coal. When it is desired to recover less than this it is not advisable to wash the whole of the gas with a smaller quantity of oil, as the effects of over-saturation then appear, and, moreover, the extraction of naphthalene falls off. The better plan is to by-pass part of the gas, and to strip thoroughly the portion passing through the scrubber. In this way the quality of the spirit is maintained, whilst at the same time a useful recovery of naphthalene is effected.

The supply of oil to the scrubbers is best regulated by means of a constant-head feed tank, as is described in Chapter V. (p. 84) for feeding the distillation plant. If a float and graduated scale be added the flow of oil may be measured easily by merely stopping the debenzolised oil pump. Such an arrangement is, however, more useful on the supply to the debenzolising plant; in that case the flow of oil to the scrubbers is regulated by keeping the levels of oil in the benzolised and debenzolised creosote tanks—as indicated by floats—constant. If it is desired to keep a more careful check on the oil supply, a meter, the internal parts of which contain no brass, may be used; whilst A. Edwards (*Proc. Junior Gas Assoc.*, 1916—17) recommends the use of a V-notch weir cut in a  $\frac{1}{8}$ -inch plate. Viscosity naturally affects the readings of such an indicator; for an average creosote and a  $45^\circ$  V-notch, Edwards gives the flow of oil in gallons per minute as  $0.8978 H^{2.5}$ , where  $H$  is the head of oil in inches above the apex of the V. The following table gives the flow of oil for each  $\frac{1}{2}$  inch of head measured by a float and graduated scale:—

TABLE 18.—MEASUREMENT OF OIL-FLOW BY WEIR.

H. Inches	0.5	1.0	1.5	2.0	2.5	3.0	3.5	4.0	4.5	5.0	5.5
Gallons per min.	0.16	0.90	2.48	5.10	10.75	14.0	20.5	28.7	38.5	50.2	63.7

The application of this method is indicated in FIG. 13, whilst FIG. 14 shows how V-notches fixed at the same level may be used to ensure even distribution of oil to two scrubbers working in parallel.

### Recirculation of Wash-oil

It has sometimes been recommended that saturated wash-oil should be recirculated over the scrubber, or over a portion of it. This should be avoided; indeed, with a scrubber of moderately high efficiency it should be quite unnecessary. If more than one scrubber be used in series the flow should be strictly according to contra-current principles, *i.e.*, the oil from the finishing gas scrubber, which is supplied with fresh debenzolised oil, should be pumped over the scrubber immediately preceding, and so on. The only circumstance which warrants recirculation is an inefficient single scrubber, in which it is impossible to attain a reasonable saturation by one circulation only. An example of this is the "Cascade" washer described on p. 39. In such a case the oil from the benzolised wash-oil tank may be recirculated through the first (gas) half of the scrubber, but never through the whole of it. In other words, it may be accepted as a principle that *gas leaving a scrubbing system must have been last in contact with fresh debenzolised oil.*

The simultaneous extraction of naphthalene will be dealt with later. Consideration of theory and of the mechanical aspects of the various forms of washing and scrubbing plant render it unnecessary to return to the subjects of temperature of washing and viscosity of wash-oil; their vital importance is obvious. Water in oil will naturally reduce its absorbing power, but its effect in this connection appears to be much greater than would be produced by a simple diluent. The presence of a considerable amount of water makes it practically impossible to debenzolise the oil completely, and this in turn affects the stripping of the gas.

### Control of the Scrubbing Process

Tests should be occasionally taken on the benzol content of the gas before and after scrubbing. Unfortunately this determination, particularly on the stripped gas, is not an easy one and is somewhat tedious. Such tests need not be frequent, however, since the quality of the gas at each point gives some indication of the working of the process, whilst the yield of crude benzol and tests on the oil give practically all the necessary information. It is advisable, though, to make such determinations occasionally in order to find the actual efficiency of the scrubbers. Tests on the benzolised and debenzolised oil must be made regularly and at least once every day, together with a distillation of the crude benzol.

### Determination of Benzol in Gas

Ste. Claire Deville's method, much used on the Continent, consists in cooling the gas to such a temperature that the vapour pressure of the contained hydrocarbons becomes negligible. Gas is passed through vacuum-jacketed apparatus in which it is

cooled to  $-70^{\circ}\text{C}$ . by means of liquid carbon dioxide. The benzols condense and may then be fractionated. This method has been modified for gases containing normal quantities of benzol, and a temperature of  $-21^{\circ}\text{C}$ . is obtained by means of a mixture of ice and salt. At that temperature the gas will only carry 23.5 grammes of benzol per cubic metre, and this constant figure is added to the amount condensed. The method is obviously inapplicable to stripped gases, which contain much less benzol than 23.5 grammes per cubic metre.

This method of refrigeration is expensive and is not well adapted to works practice. In consequence the usual test in use in this country and the United States depends on the absorption of the vapours in a solvent, just as is the case in a large-scale oil-washing plant. The gas is passed through a series of wash-bottles arranged as in FIG. 15, in which ordinary bottles are shown; glass-stoppered Dreschel wash-bottles are, however, preferable.

A benzol content of 3 gallons per 12,000 cubic feet, corresponds to only about  $1\frac{1}{8}$  c.c. of benzols per cubic foot of gas. On this account, as well as because of the low saturations which must obtain to give approximately complete extraction, it is obvious that large quantities of both gas and absorbent must be used; at least 100 cubic feet of gas should be washed, and in the case of stripped gas a larger volume is advisable. The gas is passed through the apparatus at the rate of 1 cubic foot per hour, and each bottle contains about 150 c.c. of oil. Each morning and evening the contents of the bottle first in series are drained into a half-gallon can, the bottle refilled with fresh absorbent and put on last in the series; this operation being repeated until the requisite volume of gas has been passed. The contents of all the bottles are then drained into the half-gallon vessel, the bottles washed down with a little fresh oil, and the quantity of gas passed noted, together with the average thermometer and barometer readings during the test. Whilst the gas is passing the wash-bottles should be kept cool, if necessary by immersion in water. The bulk of the absorbent is then subjected to a preliminary distillation and refractionation, as in the testing of benzolised oil (see p. 56).

The absorbent which is generally used and which is probably the most satisfactory, is either coal-tar green-oil or gas-oil; but in both cases the oil, before use, must be distilled until a thermometer in the vapour shows a temperature of  $250^{\circ}\text{C}$ ., the residual oil being employed for the test. If the preliminary distillation cannot readily be carried out, a mineral lubricating oil may be used, whilst other liquids suitable for the purpose are kerosene (after redistillation) and nitrobenzene. The advantage of nitrobenzene is its constant boiling point ( $209^{\circ}\text{C}$ .), but both this and the boiling point of kerosene are rather too low to be entirely suitable, some of the absorbent reappearing in the final fractions.

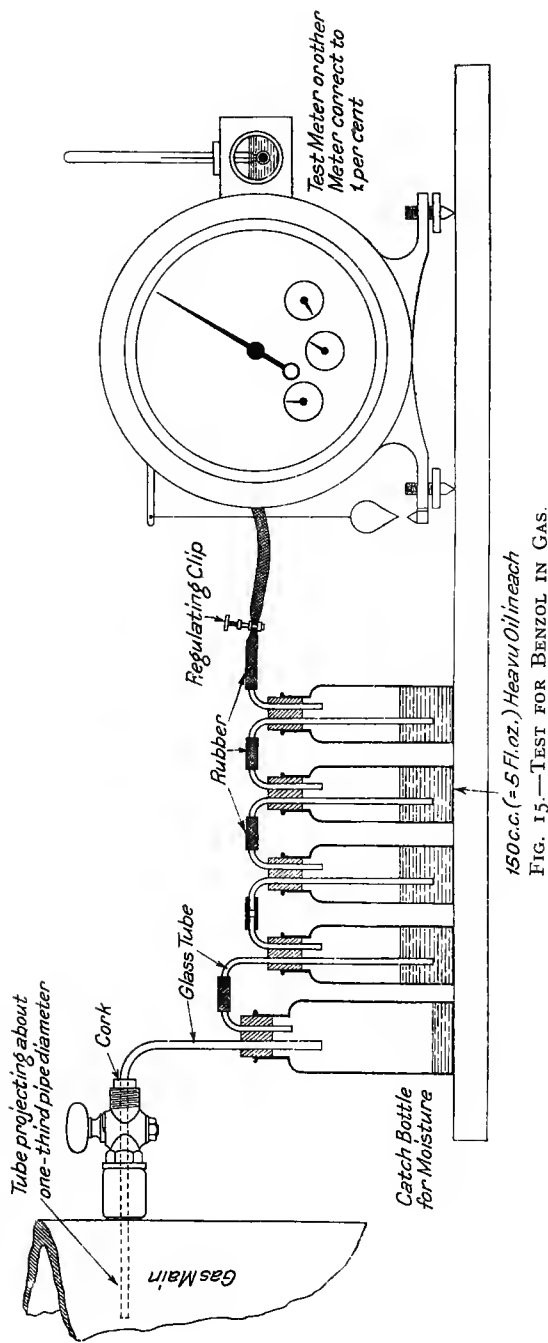


FIG. 15.—TEST FOR BENZOL IN GAS.

Nitrobenzene also is an exceedingly unpleasant material to work with. Oleic acid has also been suggested (*Jour. Soc. Chem. Ind.*, 1917, p. 25); its boiling point is higher ( $286^{\circ}$  C.) and all traces of it may be eliminated from the fractions by saponification with

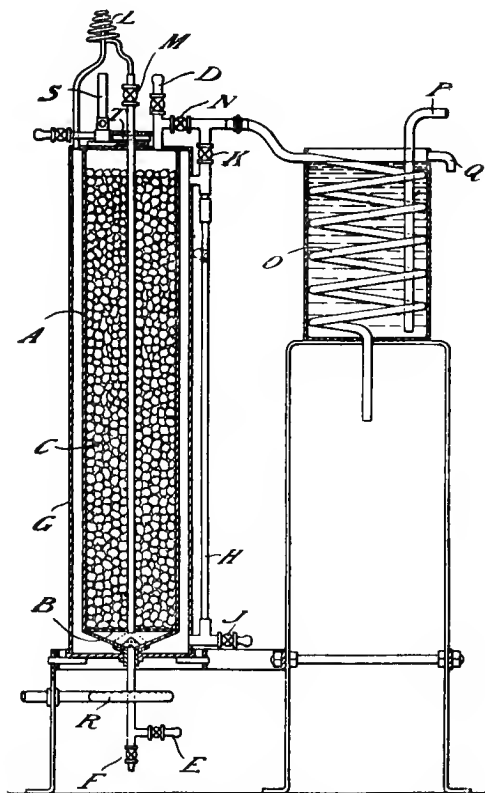


FIG. 16.—DIAGRAMMATIC VIEW OF LESSING'S BENZOL TEST APPARATUS

caustic soda. In common with lubricating oil it presents the disadvantage of a high viscosity.

The chief objections to this test are :—

- (i.) Its tedious nature and necessarily long duration.
- (ii.) The back-pressure thrown by the train of bottles, meter, etc.
- (iii.) the loss of small quantities of benzol immediately before recharging the last bottle.

In order to overcome these difficulties the test has been rendered

continuous by H. E. Copp, who describes (*Gas World*, March 17th, 1917, p. 222) a form of apparatus in which a continuous scrubber, formed from a glass absorption tower, replaces the wash-bottles. This contrivance gave a result 9 per cent. higher than was obtained with the apparatus shown in FIG. 15. T. F. E. Khead (*Jour. Soc. Chem. Ind.* xxxvi., p. 769) has successfully used a metal scrubber consisting of a number of bubbling trays, whilst R. Lessing (*Jour. Soc. Chem. Ind.*, February 15th, 1917, p. 103) has patented an original method. His apparatus, which is shown in FIG. 16, comprises a metal cylinder through which the gas is passed, the absorbing medium being held in suspension by the granular material with which the vessel is packed. After passage of the gas the same vessel serves as a still, the benzol being driven over into a condenser by the introduction of superheated steam. The absorbent remains, for the most part, among the granular packing, and the apparatus after cooling needs very little preparation for another test.

### Tests on Wash-oil

There is a very regrettable absence of any standard methods for determining the benzol content of wash-oil. As this test is more frequently performed on the debenzolised oil, contractors are naturally inclined to adhere to a method—such as a simple retort distillation—which gives a low result, whilst inertia on the part of those responsible is the main reason for the continued use of such a test. This determination is probably the most important one to be made in connection with benzol recovery, and whilst it is essential that both benzolised and debenzolised oil shall be analysed frequently and regularly, it may be said at once that such tests, if done by an unreliable method, are valueless and a mere waste of time. The three essentials for the test to be reliable are :—

- (i.) A representative sample must be obtained.
- (ii.) A large quantity must be distilled.
- (iii.) Water must be eliminated before the final fractionation.

The exercise of an ordinary amount of care will ensure the fulfilment of condition (i.). As to the second at least one litre (preferably two litres) of benzolised oil, and at least two litres of debenzolised oil must be taken for a test. This quantity is distilled preliminarily in a metal still of which there are several suitable types available. The best are probably those designed by Dr. H. G. Colman (FIG. 17) and G. Weyman (FIG. 18). In each of these stills priming and "bumping" are avoided by applying the heat at first to a relatively small depth of oil. In the former apparatus a ring burner surrounds the still, and is fixed at the commencement about  $\frac{1}{2}$  inch below the surface of the oil. The consequent absence of convection currents enables

the top layer of oil to be completely dehydrated, the ring burner being gradually lowered to the bottom of the still, after which the distillation is completed by a Bunsen burner under the base. With the apparatus shown in FIG. 18, distillation is commenced by a burner placed under the raised end, the burner being moved gradually to the lower end in a similar manner.

Distillation is continued until a thermometer in the vapour registers about  $200^{\circ}\text{C}$ ., when the receiving cylinder is removed. The remaining distillate up to  $230^{\circ}\text{C}$ . is collected in a flask, water being run out of the condenser at about  $210^{\circ}\text{C}$ . to avoid stoppage of the latter by solid naphthalene. The reason for keeping the two fractions separate is also to avoid the presence of this solid along with the water and oil, naphthalene crystals interfering

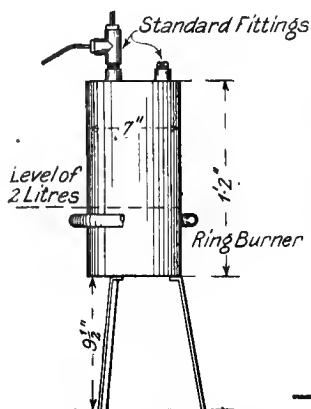


FIG. 17.—COLMAN'S STILL.

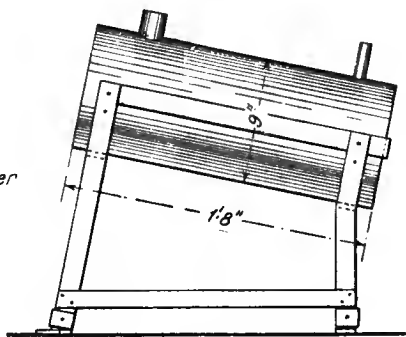


FIG. 18.—WEYMAN'S STILL.

considerably with separation. After reading off the volume of water in the first distillate, the water is carefully separated, and the oil run into the flask containing the higher fraction. This is fitted with a 12-bulb Young's still-head or other suitable fractionating column, and the liquid is distilled at the rate of about 1 drop per second. Distillation is stopped at  $160^{\circ}\text{C}$ . (or other convenient temperature if any particular fraction be desired) and the volume read off. This gives the proportion of crude benzol up to  $160^{\circ}$ , or of "washable products" in the oil originally taken. If the amount of 65's crude benzol in the oil be required, this is given very closely by dividing the fraction up to  $160^{\circ}\text{C}$ . by 0.8.

Tests for the viscosity of oil have been described on p. 46, and specific gravity may be determined by any well-known method of the degree of accuracy desired.

### Estimation of Naphthalene in Oils

Several methods are available for this determination all depending on the combination of the hydrocarbon with picric acid to give naphthalene picrate. An indication of the naphthalene content of the oil is given by pressing and weighing the solid which separates on cooling a suitable fraction, say  $180^{\circ}$ — $230^{\circ}$  C., of the oil. Owing to the residual oil being saturated and to the distillation of some naphthalene into the earlier fractions, this rough test gives a low result.

In the usual test a weighed quantity of the oil is mixed and shaken with about twenty times its bulk of glacial acetic acid, and the resulting solution made up to a known volume. An aliquot portion is filtered off and sufficient of a cold picric acid solution added to precipitate all the naphthalene. After standing for an hour the mixture is poured into a hard filter paper and filtered with the aid of a filter pump. The precipitate is washed with cold picric acid solution and left for a time with the pump still working. In this way it is possible to obtain a nearly dry cake of naphthalene picrate, which is transferred to a beaker and boiled with water. The boiling decomposes the picrate, distils off the naphthalene and separates any tarry matter. If this be present another filtration is necessary. The final filtrate, which contains the picric acid originally in combination with the naphthalene, is titrated with decinormal sodium hydroxide, using phenolphthalein as an indicator.

1 c.c. of decinormal soda = 0.0128 gramme naphthalene.

Knublauch determines naphthalene in tar-oils by direct titration of the picrate, which is precipitated from alcoholic solutions of the sample and of picric acid. Precipitation is complete if the resulting solution contains not more than 10 per cent. of alcohol and at least 0.2 per cent. of picric acid; or less than 12.5 per cent. of alcohol and at least 0.3 per cent. picric acid.

A quantity of the oil containing 0.1—0.2 gramme of naphthalene is weighed into a 200-c.c. flask, and to it are added 15 c.c. of absolute alcohol, and picric acid equal to  $2-2\frac{1}{2}$  times the weight of naphthalene present. The mixture is heated to  $60^{\circ}$ — $65^{\circ}$  C. until all is dissolved, cooled, and the volume made up to 200 c.c. with a 0.3 per cent. aqueous solution of picric acid. After one hour the precipitate is collected on a 10-cm. smooth filter paper and washed with a 0.2 per cent. solution of the acid. The paper and its contents are transferred to a beaker with 50—80 c.c. of water, and titrated with decinormal soda, using methyl orange as indicator. A deduction of 0.2 c.c. of soda is made for the picric acid solution retained by the filter paper.



### Determination of Anthracene

Anthracene,  $C_{14}H_{10}$ , is determined by the anthraquinone test, in which it is oxidised to anthraquinone,  $C_{14}H_8O_2$ , and weighed as such. It is convenient to distil the oil and perform the test on the anthracene fraction, say  $300^\circ - 380^\circ C$ . Such a quantity of this fraction as is expected to contain about  $\frac{1}{2}$ —1 gramme of anthracene is boiled with 45 c.c. of glacial acetic acid under a reflux condenser. To the solution is added, very gradually, a mixture of 15 grammes of chromic acid dissolved in 10 c.c. of glacial acetic acid and 10 c.c. of water, the addition extending over two hours. The mixture is allowed to boil for a further two hours and then to stand for twelve hours. It is subsequently poured into 400 c.c. of water, allowed to stand for a further three hours and filtered.

The anthraquinone on the filter is washed first with water, then with hot dilute soda, and finally with hot water. It is transferred to a dish, dried at  $100^\circ C$ ., and digested with ten times its weight of fuming sulphuric acid which dissolves the precipitate. The solution is allowed to remain in a moist atmosphere for twelve hours, and finally mixed with 200 c.c. of water. This dilution reprecipitates the anthraquinone, which is filtered off, washed with water, dilute alkali and again water, and dried at  $100^\circ C$ . After weighing, the precipitate is carefully transferred to a tared crucible and ignited. The weight of ash remaining is deducted from the weight of reprecipitated anthraquinone, the result giving the amount of that substance corresponding to pure anthracene in the sample taken.

Weight of anthracene = weight of anthraquinone  $\times 0.8558$ .

## CHAPTER IV

### THE DEBENZOLISING PLANT

DEBENZOLISING plants may, in general, be divided into two classes—steam-heated and direct-fired—the former type being by far the more usual and, where a good steam supply is available, the more satisfactory, economical and easily controlled. Tar dehydration plants have been used for the purpose fairly extensively during the war, and some of them have been adapted for debenzolising by the addition of open steam jets, dephlegmators, etc. After considering the general lay-out and construction of the plant it is proposed to discuss the design of each part in some detail, following the course of the ingoing benzolised oil, and finally to describe some typical plants of each type.

#### Lay-out and Position of the Plant

The general arrangement of a typical crude benzol plant has been indicated on p. 9 and in FIG. I. As regards general lay-out of the apparatus, much will depend on convenience and on the arrangement of the existing portions of the works. Every effort should be made to take advantage of differences in ground levels in order to reduce the necessary pumping as far as possible. For example, the writer was connected with the erection of a benzol plant at a works in which three distinct levels occurred, the scrubber being on the lowest. The debenzolising plant was erected on the middle "step," where also were the coolers, and adjoining these a pit containing the debenzolised oil tank. In a similar pit beside the scrubber was the benzolised oil tank, and a pump was used to transfer oil intermittently from this tank to a tank situated on the highest level, and feeding the distillation plant. By having a fairly large tank for this purpose pumping was reduced to one hour per shift. Apart from this consideration, the plant should be so arranged as to require as little pipe work as possible, and, in order to avoid heat loss, the heat exchangers, preheaters and still should be placed closely together.

Where the scrubber is at some distance from the debenzolising plant it is advantageous to erect the coolers and debenzolised oil tank near the former, where steam and water supplies will allow. In this way the oil pipe between heat exchangers and coolers is converted into an air-cooler and water is saved as a result. The debenzolising plant should be placed as near to the steam boilers as possible, consistent with other requirements.

### Foundations

Little need be said on this subject except to point out that in all chemical plant, involving much pipe work and flanged joints, the foundations should be made thoroughly substantial. It is false economy to cut down the foundations to the lowest possible figure, as the slightest subsidence of any part of the plant will usually result in sprung joints or broken pipes and leaks. Creosote leaks, besides being wasteful, are particularly objectionable. Where any doubt is felt as to the solidity of the ground, foundations should be reinforced by horizontal layers of old rails or similar material. As regards housing the plant, it is scarcely necessary to erect a new building for this purpose; if an old one is available it should be utilised, whilst a covering of corrugated iron is a useful protection for exposed situations.

### General Construction

Where crude gas is washed it is essential that every portion of the plant coming into contact with warm or hot oil, or with benzol vapours, should be constructed of cast iron, as this is much less liable to corrosion than wrought iron or steel. In such cases

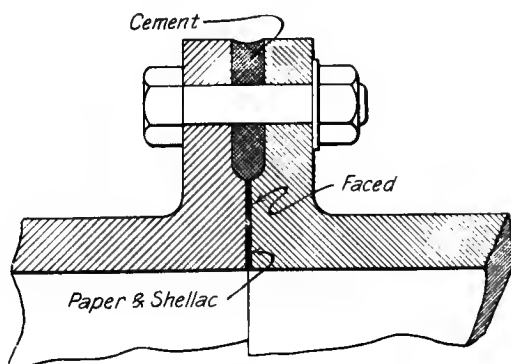


FIG. 19.—ANNULAR-FACED FLANGE JOINT.

wrought-iron preheater coils have been destroyed in a week or two. If the gas be purified before oil washing, such parts as heat exchangers and preheaters are more conveniently made in wrought iron or steel. These materials are more efficient conductors of heat owing to their being comparatively thin, whilst their greater elasticity minimises the risk of fracture through unequal expansion. Stills, when of the bubbling-tray type, are constructed for convenience in cast iron. Good sound castings are essential throughout; wash-oils and benzol have much

greater powers of penetration than water, and a serious "weep" often makes its appearance where not the slightest flaw is visible. Such cases are best dealt with by drilling and tapping, followed by the insertion of a plug. Iron cements, etc., are seldom satisfactory owing to the smallness of the perforation and to the difficulty of obtaining clean surfaces where oil has been passing.

For the same reason joints should receive very careful attention. All flanges should be faced, and the best material for such joints is then undoubtedly brown paper coated with shellac varnish. A very safe and reliable form of joint is shown in FIG. 19. It contains an annular facing strip forming the inner portion of the flange. A joint is made on this with brown paper and shellac, the bolts inserted and tightened up, and, finally, the space between the flanges and around the bolts is filled by running in neat cement. This joint is particularly serviceable in protecting the bolt from the corrosive action of the oil.

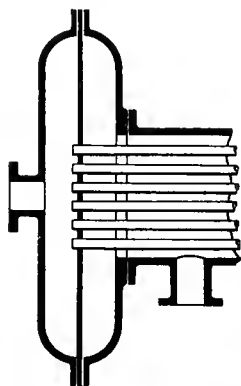


FIG. 20. — EXPANSION BOX ON TUBULAR HEATER.

Many parts of the plant are subjected to unequal heating, and allowance must be made for expansion, especially in cast iron. Stuffing-box expansion joints are never satisfactory, and the best way out of the difficulty is to ensure that the parts should be fixed at one end only; as an example, reference may be made to FIG. 22, p. 67. In the case of coils this precaution is not necessary, but in tubular preheaters one of the tube plates should be formed into a flexible diaphragm in a steel expansion box of large diameter. This construction will be understood from FIG. 20.

Much trouble is caused on badly-designed plants by the occurrence of air- or vapour-locks. To avoid these any portion of the plant which forms an "inverted U" should be provided with a vent pipe at its highest point. Such vent pipes on the debenzolised oil system may be open to the air; on benzolised oil, however, loss must be avoided by connecting them into the top of the still or, better, into the vapour pipe between the still and the condenser. In the latter case they should be taken into the top surface of the vapour pipe, in order to prevent the return of liquid condensates to the oil. Vent pipes on the benzolised oil should be reduced to a minimum by ensuring that all hot oil connections have a slight rise towards the next piece of apparatus, and that the oil outlet is situated at the highest point of any heating member. By the latter precaution gas pockets—frequently the cause of local corrosion—are avoided.

Vessels in which oil is heated are very liable to choking by the formation of solid deposits. Every portion of the apparatus should, therefore, be provided with hand-holes, and with a sludge cock at its lowest point. The omission of these frequently causes trouble in clearing a blockage; and it has at times been necessary to dismantle the plant when the removal of one or two hand-hole covers would have sufficed.

In some cases preheaters are fitted with gilled steam pipes. They are certainly more efficient than plain pipes when clean, but the author's experience indicates that they are not advisable in this connection. The solid deposits referred to in the preceding paragraph invariably settle out between the gills, which form very effective keys, and owing to the absence of convection the layer of "mud" succeeds in lagging the steam pipes, with a considerably reduced heating power as a result. Gilled pipes are costly and the extra expense can be more profitably incurred by putting in a longer run of plain pipes, which, in most preheaters will give the same heating surface coupled with greater intimacy of contact, and a minimum of trouble through deposits.

### Connections and Steam Supply

It has been stated that oil connections should never be less than 2 inches in diameter, and they may vary from this size up to 4 inches on large plants. This applies to pipes conveying cold oil or hot debenzolised oil. Where a pipe contains hot benzolised or partly-benzolised oil this diameter should be exceeded. For example, the connection between preheater and still conveys oil at about 120° C. and containing some benzols. Such a pipe must be capable of taking the requisite quantity of oil in the form of a foam together with a considerable quantity of vapour, and should be of 4-inch diameter where the other connections are 2-inch. This is particularly important where the addition of a gas off-take from the preheater has been avoided by taking the oil outlet from its highest point.

All benzol connections should have satisfactory electrical connection with earth. It appears probable that the friction caused by the passage of benzol at a rapid rate through an iron pipe gives rise to an electrical potential, which may in extreme cases cause sparking. When electrical plant is in the vicinity every care should be taken to prevent sparking through leakage. The author once had the unpleasant experience of a spark between the man-lid of a tank wagon and the benzol delivery pipe (fortunately before starting the benzol pump!) due to a "short" in a neighbouring electric hoist.

Dry steam at high pressure is essential to good working, and it must be repeated that, on this account, the debenzolising plant should be situated as near the boilers as is practicable. The steam pressure should be maintained steadily at a high figure;

100 lbs. per square inch should be aimed at. Very few plants will work satisfactorily at much less than 60 lbs. Separators are useful when wet steam is unavoidable, and a superheater is an advantage in extreme cases.

### Lagging

All steam pipes must be well lagged, and the cost of such lagging is more than repaid in a very short time. Any condensation in the steam service means more water to be evaporated in the still, and consequently an increased fuel consumption. Wet steam, moreover, causes priming in the still, especially in pot-stills.

The importance of insulation cannot be overrated. In addition to the steam supply all heated portions of the plant (except the heat exchanger, which will be referred to later) must be effectively lagged, and for this purpose any good boiler covering is suitable. Those composed of asbestos and magnesia are probably the best, for, although their first cost is high, such compositions may be remixed and used repeatedly after stripping off for repairs, etc. The efficiency of any type of lagging depends upon its porosity and the contained air-spaces. It must, therefore, obviously be kept dry, and accordingly all lagged surfaces should be treated with two or three coats of tar varnish. If a part of the apparatus is particularly exposed to the weather, a layer of webbing or canvas should be bound over the lagging before applying the tar varnish.

### Steam and Water Economy

It may be said at once that the use in the still of open steam derived from the preheater exhaust is the very reverse of economy. In a number of cases engineers have "economised" by taking their open steam supply from the outlet of the preheater coil, but it must be realised that if the steam is to do any useful work in the latter some of it must condense; and this arrangement will result not only in pumping water into the oil, but also in losing the drying effect of the subsequent expansion of the steam. Steam can only be saved by ensuring its high pressure and dryness, and by attention to counter-current principles and intimate contact in the preheater.

The possibilities of economising in water vary with its source and with the arrangement of the plant. Distribution and time contact in condensers and coolers should receive attention, and some saving may be effected by leading the waste water from the condenser over the oil-coolers. If water is scarce or expensive it may be cooled by zig-zagging along the base of the pit containing the storage tanks, by a simple cooling tower, or by a spraying device; whilst a useful source is a gas-holder tank. Cold water may be pumped continuously from the bottom of the tank and when warm returned to the top.

### Design of the Plant

In discussing the design of each portion of a debenzolising plant it may be stated that contractors usually allow for the circulation of 60 gallons of oil per ton of coal, unless any other figure is specified. Scrubbing consists in the transfer of a hydrocarbon from one fluid to another, and both heating and cooling processes entail a similar transfer of heat. All parts of the distillation plant should therefore be designed on counter-current lines wherever possible. In order to be some guide in designing a plant, the heating or cooling surface required in each portion has been stated; but it must be recognised that these figures are only approximate, and vary with such factors as steam pressure, temperature of cooling water and thickness of material. Thus a wrought-iron or compo. condenser coil is more efficient than one of the same size in cast iron.

#### *Heat Exchangers*

The usual heat-interchanger or economiser is an oil-to-oil apparatus, but vapour-to-oil exchangers are also frequently used, either alone or in conjunction with the former. An oil-to-oil exchanger should always be adopted, as it not only conserves heat by transference from the debenzolised to the benzolised oil, but also saves a considerable amount of cooling water. It may consist of a coil in a tank, or be annular or tubular. The last is, on the whole, probably the most satisfactory, but it must be placed vertically. In any heat exchanger it is very difficult to ensure full contact between the oil and the tubes or pipes, and the distribution of heat is often uneven in consequence. Convection should be utilised to increase the time-contact as far as possible, and vent pipes must be fitted wherever there is a possibility of an air-lock.

These points are illustrated in FIG. 21, which indicates the arrangement which gives the best results in practice. If such a piece of apparatus be fixed horizontally it is usually found that the distribution of heat is poor, and that the shell is divided into hot and cold zones by, roughly, a diagonal of its section. It must be remembered that the flow of oil through the plant is comparatively small, and that the topmost two or three tubes will deal with the whole of it. Plugs with small holes have sometimes been fitted to the ends of the tubes, but are usually liable to become choked with solid matter resulting in a worse state of affairs than before.

The annular heat exchanger consists of a series of double pipes, the inner one conveying the hot oil through the cold ingoing oil, whilst the coil type resembles a worm condenser. Heat exchangers are always thermally inefficient owing to low time-contact, and on this account should always be so constructed as to have the hot debenzolised oil on the outside, and the exchanger should

not be lagged. In this way an amount of air cooling of the oil is obtained which materially assists the coolers.

As previously mentioned, vent pipes must be fitted, and all joints must be well made internally in order to prevent short-circuiting. If this is suspected it may be at once verified by estimating the benzol content of debenzolised oil entering and leaving the shell, good average samples being taken. The heat-interchanging surface, when this appliance is used alone, is about 1.0 to 1.2 square feet per gallon of oil debenzolised per

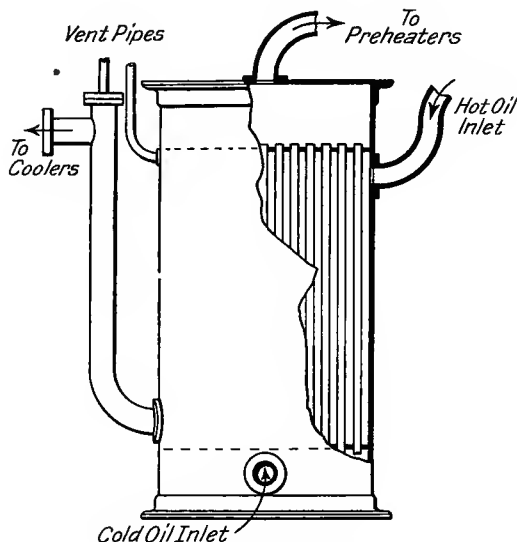


FIG. 21.—ARRANGEMENT OF TUBULAR HEAT-EXCHANGER.

hour ; if a vapour-oil exchanger is also used this may be reduced to 0.8—0.9 square foot.

Vapour-to-oil heat exchangers, or primary condensers, are of somewhat doubtful utility. They necessitate more or less complicated pipe connections, and, whilst they certainly tend to economy of condensing water, they necessarily limit the effectiveness of the oil-to-oil apparatus. When primary condensation is carried out in connection with the elimination of naphthalene such condenser should be cooled by water and not by oil, in order to get greater control. These heat exchangers may be tubular or of coil form, the cold benzolised oil passing through them before proceeding to the oil-to-oil economiser. The heating surface may conveniently be 0.3—0.4 square foot per gallon of oil per hour.



*The Preheater*

This is a most important part of the plant and should be capable of raising the maximum flow of oil to at least  $135^{\circ}\text{C}$ . This is higher than the normal working temperature, but in this as in the whole of the plant, a margin should be allowed for dealing with a high water-content or viscosity of the wash-oil. The preheater must be designed with a view to securing maximum time-contact and passage of the oil over the heating surface, whilst at the same time using as little steam as possible. Several types of preheater are available.

When clean gas is scrubbed a plain wrought-iron coil is most effective; but if any ammonia or hydrogen sulphide are present the heater must be of cast iron. Heating coils in this material are not very efficient; it is difficult to procure sound castings throughout, and internal joints are apt to leak. On this account

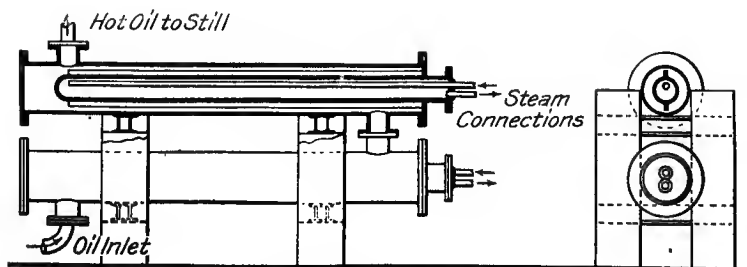


FIG. 22.—ANNULAR PREHEATER.  
(Chemical Engineering Co.)

the "annular" or "loop" forms of heater are preferable. These are illustrated in FIGS. 22 and 31 respectively, whilst FIG. 33 shows the construction of the coil preheater. A heating surface corresponding to 0.3 square foot per gallon of oil per hour will be found suitable for a cast-iron preheater, with steam at 80—100 lbs. per square inch and oil leaving the heat exchangers at about  $60^{\circ}$ — $65^{\circ}\text{C}$ . If the heating elements are constructed in wrought iron or steel, the more rapid conduction of heat through the thinner metal will allow a reduction to 0.2—0.25 square foot. This surface represents that actually available for heat transmission, and therefore does not include any gills or other devices. Gilled pipes, as previously explained, should be avoided in preheaters.

Steam connections and coils must be tight, and should be arranged so that the regulation of the steam is effected *after passing through the heater*. In this way full boiler pressure is maintained in the coils, and maximum duty results. Regulation of the steam may be accomplished either by a valve or by a good

steam-trap, or both. When more than one preheater is used they may be connected in series as regards steam, as well as oil, the direction of flow being contra-current. It is doubtful, however, whether much advantage is gained thereby (see FIG. 22) over the provision of a separate steam service to each; but where this is the case the exhausts should be taken to separate valves or traps. Preheaters must always be provided with gas off-takes unless the heated oil leaves by a pipe of large diameter situated at the highest point.

Direct firing is sometimes resorted to for this operation and will be discussed later (see p. 79).

### *The Still*

The function of the still is to subject the hot oil to the action of an ascending current of steam and vapours, whereby the

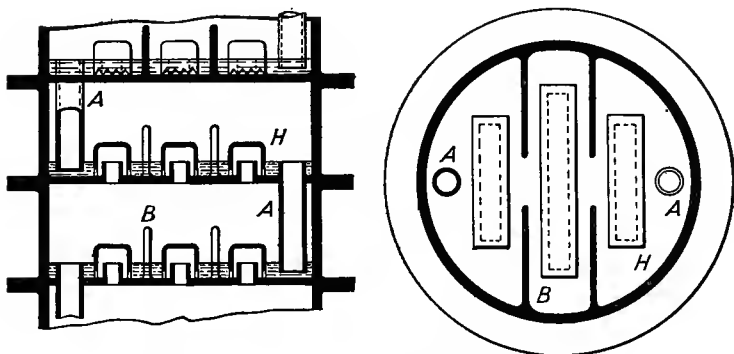


FIG. 23.—TRAYS OF A BUBBLING-HOOD STILL.

remaining benzol is expelled and carried over into the condenser. It must necessarily, therefore, provide intimate contact for as long a period as possible. Several forms of still are available, but it will suffice to describe the two most efficient and commonest ones—the bubbling-hood type and the column still.

A common form of bubbling-hood still is shown in FIG. 23. Condensed products flow downwards from tray to tray through the sealed overflow pipes A, A, and the ascending vapours are forced to bubble through the liquid under the serrated hoods H. Baffle plates B are cast in each tray to ensure length of travel and intimate contact. FIG. 24 shows a similar tray in which circular bubbling hoods are used.

Stills are built up of from six to eighteen of these trays, the hot oil being led into one near the top, and one or two trays above the oil inlet being utilised for purposes of fractionation. These stills vary in diameter from 2 feet 6 inches to 4 feet 6 inches,

and one of the latter diameter will deal with as much as 1,500 gallons of wash-oil per hour. The gas passages in each tray should total to 0.2 square inch per gallon of wash-oil per hour, and the overflow pipes should be of ample diameter as these limit the capacity of the plant.

The general arrangement of the still is clearly shown in FIG. 30 (p. 74). Open steam is introduced by means of a perforated pipe in the bottom chamber, and here also is sometimes fitted a closed steam coil for the purpose of ridding the oil of any traces of water. This should not be necessary if the preheaters are sufficiently powerful, as the latent heat of the benzol forms only a small proportion of the total heat of the oil. It is, however, an advantage where there is any possibility of water trouble.

The column still is illustrated by the "Southport" plant (FIG. 34, facing p. 80) and by the "Wandsworth" plant (FIG. 33, p. 78). It consists of a cylindrical vessel packed with earthenware rings, Raschig rings or coarse iron borings, and the oil is led in at a point rather more than half-way up the column. Open steam is admitted at the base, and the one vessel serves the double purpose of still and fractionating column.

Fractionation to a certain extent may be advisable on a crude benzol plant, especially where the spirit is sent away for rectification, but even then it should not be carried to excess. A separate dephlegmator for naphthalene extraction is preferable with only a short fractionating column added to act as a baffle chamber in the event of priming. Thermometers must be fitted in the oil entering and leaving the still. Without them satisfactory working is impossible.

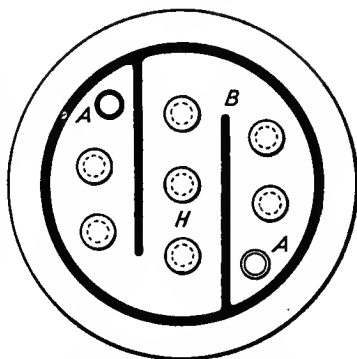


FIG. 24.—STILL WITH CIRCULAR BUBBLING HOODS.

Fractionation is preferable with only a short fractionating column added to act as a baffle chamber in the event of priming. Thermometers must be fitted in the oil entering and leaving the still. Without them satisfactory working is impossible.

### *The Condenser*

After leaving the still the benzol vapours and live steam pass to the condenser, which may be a coil in a tank of water or of the tubular or annular counter-flow types. The last-named is illustrated in FIG. 32 and is probably the most efficient, though expensive. Tubular and coil condensers are shown in FIGS. 25 and 26, in which I and O are the water inlet and outlet respectively, V the vapour inlet, and B the benzol outlet. Condenser tanks are usually constructed in wrought iron or mild steel

though during the war some have been built in cast iron, and even in wood coated internally with tar.

With ammonia or other impurities present a coil should be chosen and constructed in cast iron, but when dealing with purified gas, wrought iron or compo. coils are cheaper and more efficient. In such a case better distribution and higher efficiency may be attained by the use of a double coil, one being situated within the other. The water inlet should, of course, be at the bottom of the tank, with an overflow at the top, and a drain cock should be added for emptying the tank.

The surface area required for condensing depends upon the

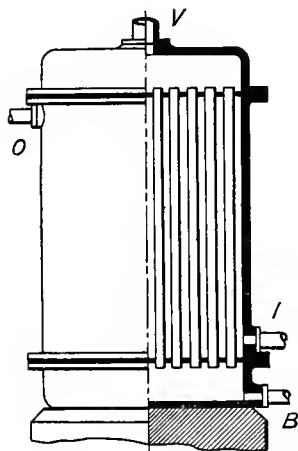


FIG. 25.—TUBULAR CONDENSER.

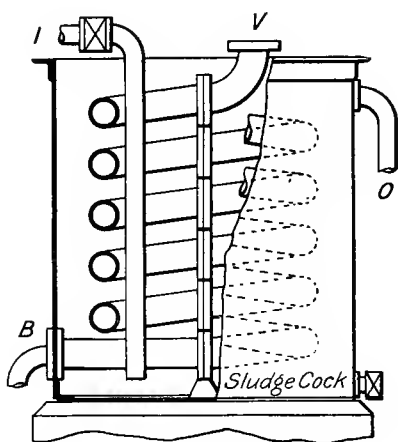


FIG. 26.—COIL CONDENSER.

presence or absence of a vapour-to-oil heat exchanger, and also upon the quality of benzol produced since the amount of live steam varies with this. A cast-iron coil, working without such a heat interchanger should have 0.6 square foot of cooling surface per gallon of oil per hour, whilst one of wrought iron or compo. pipe need have only 0.4–0.5 square foot. The presence of a primary condenser cooled by oil reduces these figures to 0.3 or 0.4 square foot.

### *The Separator*

This is the vessel in which the crude benzol is freed from the water condensing with it, and derived partly from the wash-oil, but mostly from the open steam admitted to the still. The body of the separator should be of moderate size and deep rather than wide, in order to give plenty of height for the water to settle out. A frequent arrangement is a cast-iron pot, 1 foot to 18 inches

in diameter and 2 feet 6 inches deep. It is provided with a cover carrying the inlet pipe, which is connected to the condenser outlet, and also a vent pipe. Alternatively the inlet pipe may be introduced at the side under the flange. This pipe should have a gradual fall from the condenser and should not be sealed.

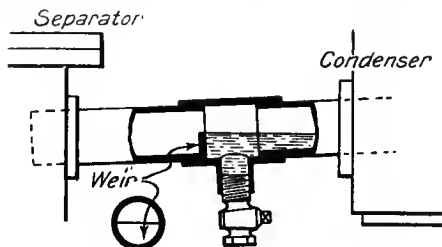


FIG. 27.—COCK FOR SAMPLING BENZOL.

Any seal here throws back pressure on the still and causes an intermittent flow of liquid owing to rushes of vapour, the evolution of permanent gases, and to the "pendulum" movement of the entrapped liquid. Since it is essential to be able to test the benzol being produced at any given moment, facilities for sampling the condensate should be provided on this pipe, thus avoiding the "lag" due to the bulk of liquid in the separator. This is

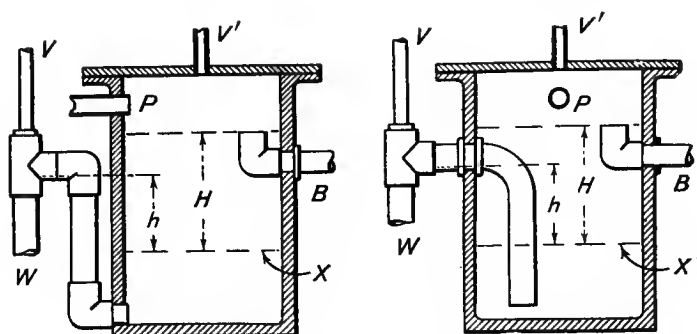


FIG. 28.—AUTOMATIC SEPARATORS.

best accomplished by inserting a small baffle or weir in the bottom of the pipe, immediately preceded by a small cock. The arrangement is shown in FIG. 27, and besides allowing for the taking of "snap" samples ensures the whole of the distillate passing through the cock, so that the proportion of water to benzol may be readily ascertained. This proportion gives the most useful guide as to the correct use of open steam.

Separators should always be made automatic, although some

forms on the market even now require constant attention to the water-cock. Advantage may be taken of the difference in specific gravity between benzol and water, and the positions of the respective outlet pipes fixed accordingly at different levels. FIG. 28 shows two suitable forms of separator (the differences in level being exaggerated) in which P is the inlet pipe, B and W the benzol and water off-takes respectively and X the line of separation of the two liquids. In designing such a separator it is obvious that a column of water of height  $h$  balances a column of benzol of height  $H$ . Taking the mean specific gravity of benzol as 0.88, therefore,  $h \div H = 0.88$ . This value is so fixed that X occurs about midway between B and the base of the pot. Thus, for a crude benzol of this gravity, and with X 14 inches from the bottom, the difference between  $h$  and  $H$  would be about 1.9 inches. The separator would be quite automatic for any probable quality of benzol, since a variation of 0.02 in specific gravity would cause X to rise or fall only about  $2\frac{1}{2}$  inches. If desired to adjust for such variations a movable elbow may be added to the benzol pipe as shown; this, however, is an unnecessary refinement. In order to prevent siphoning it is necessary to leave the water pipe W in communication with the air at its highest point, and a vent V is fitted.

### Oil Coolers

The debenzolised oil must be cooled by water. Theoretically this operation could be carried out by heat-interchange entirely, but the apparatus for this, and also for air-cooling, would be so large and costly as to be impracticable. Oil coolers may be immersed or evaporative. The former consists of a coil in a

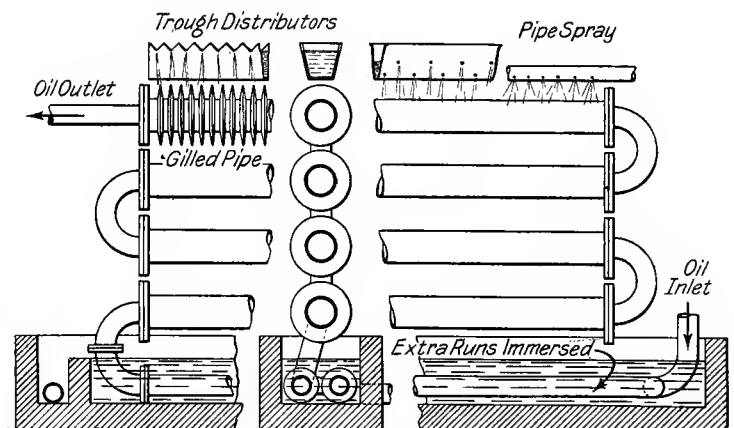


FIG. 29.—OIL COOLERS.

tank of water and is comparatively inefficient and costly unless large quantities of cheap water are available. They are obviously limited to the addition of sensible heat to the water, whilst the second type utilises the latent heat of evaporation. Spray coolers merely consist of several runs of pipes, either gilled or plain, over which water is allowed to trickle; both types are illustrated in FIG. 29, which also shows three methods of distributing water over the pipes. The even distribution of the water is a most important point, and the extra cost of gilled pipes is practically thrown away, if the whole of the gills, as well as the intervening portions of the pipe, are not kept continually wet. An allowance of at least 1.2 square feet (irrespective of gills) per gallon of wash-oil per hour should be made with cast-iron coolers. In wrought iron the area may be only 1 square foot per gallon.

Coolers are usually erected over shallow brickwork or concrete tanks which serve to collect and carry away the water. A useful addition to the cooling capacity of the plant is made by a run or two of 3-inch wrought piping along the bottom of this tank, which is kept full of water by a small dam at one end. The hot oil is led first into this extra coil, and a greater absorption of heat per gallon of water thereby obtained. This arrangement is also shown in FIG. 29.

Oil coolers should always be fitted with a by-pass connection, and the author has added many, although he has very rarely seen one put in by a contractor. There is always the risk of a stoppage occurring in one of the pipes, and it is therefore advisable to have some means of diverting the course of the oil. It may also happen that, in winter, the coolers are too drastic even without water. The use of a by-pass is then appreciated, and much trouble through condensation of water in the scrubbers avoided. For the former reason, also, coolers should be provided with a run-off cock at the lowest point. Readers who have dismantled a cooler filled with creosote will appreciate this point.

### Typical Steam-heated Plants

There are many types of benzol recovery plant on the market, the majority of which are efficient, and which vary mainly in details of design. It is not possible to describe more than a few examples, and the author has chosen those plants of which he has had actual working experience, and which, at the same time, demonstrate differences in constructional details.

Wilton's (Chemical Engineering Co.'s) plant is shown diagrammatically in FIG. 30.

This plant is constructed throughout in cast iron. The heat exchangers are both vapour/oil and oil/oil, the latter being in the form of coils immersed in tanks of hot debenzolised oil, whilst the former is tubular. Benzolised oil from the pump

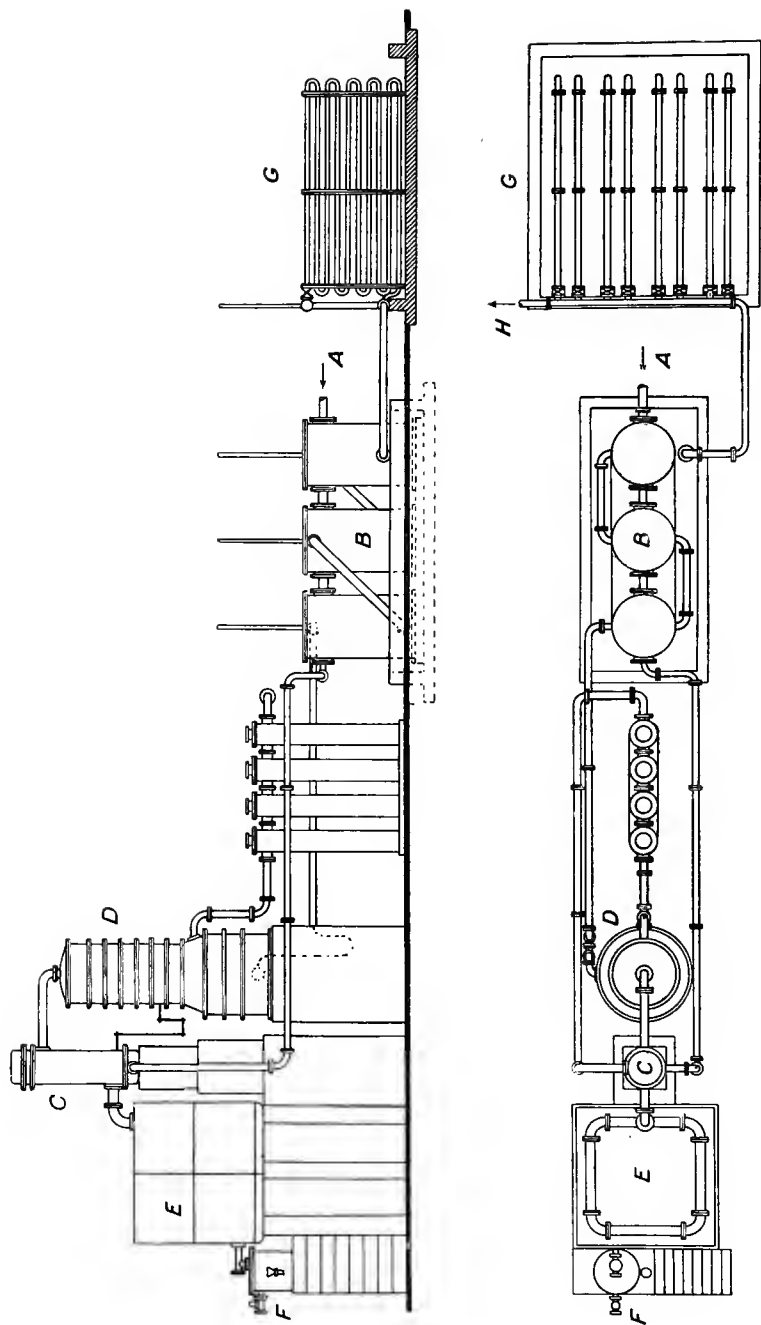


FIG. 30.—WILTON'S DEBENZOLISING PLANT (*Chemical Engineering Co.*)

A, Benzolised oil inlet; B, Oil to oil heat-exchanger; C, Vapour to oil heat-exchanger; D, Still; E, Condenser; F, Separator; G, Coolers; H, Debenzolisng oil outlet.



enters the oil/oil heat exchangers, passing through the coils in series and thence through the vapour/oil apparatus to the preheaters. These are of the cast-iron annular type, and are placed vertically. The horizontal design shown in FIG. 22, and adopted on this firm's later plants is a great improvement. The oil, on leaving the preheaters, passes into the still which is of the bubbling tray type, and this, together with the cast-iron coil condenser and the separator, needs little further description. The benzol leaves the separator through a calibrated sight feed, which gives at a glance the approximate make per hour.

Several trays are left between the top of the still and the hot oil inlet, and these serve as both priming chamber and fractionating column. Open steam enters the bottom section of the still, which also carries the debenzolised oil outlet pipe and a thermometer case. The cast-iron coils in heat exchangers and condenser are formed of special semicircular segments, the flanges of which constitute distance pieces when the coil is built up. The oil-coolers are well-designed, and consist of 8 sections each containing 10 lengths of plain cast-iron pipe, sprayed with water from a perforated pipe above. The oil inlet to each section is formed by a compo. bend which prevents fracture due to unequal expansion.

R. and J. Dempster's debenzolising plant, though similar in principle, exhibits several interesting differences in detail (*see* FIG. 31). The heat exchangers are of wrought iron and are tubular. These were formerly placed horizontally, but the vertical position is now adopted owing to the more even distribution of heat resulting. Two heat exchangers A, A, are shown in series, and from these the oil passes to the preheater B which is of the "steam loop" type. It consists of a mild steel vessel of rectangular section, into which project a vertically-placed set of steam loops connected up in series. The number of sets of such loops varies with the size of the plant from one to four, two being shown in FIG. 31. These loops are of cast iron, gilled, and free to expand, and the steam traverses each set in a downward direction, the oil passing upwards through the casing. The still C which receives the oil leaving the preheater is built of cast-iron bubbling trays and is surmounted in the larger plants by a fractionating column D containing perforated plates. The oil enters and leaves the still through baffle pots H, H, and the bottom section contains one or more dry-steam loops, as well as the open steam distributor. Both still and column are fitted with sludge cocks.

The condenser E is tubular and of wrought iron or mild steel, and the benzol and water leaving it are divided in a cast-iron rectangular separator F carrying a luted lid and glass dome through which the sight-feed is visible. Finally, the oil-coolers G comprise several runs of large diameter gilled cast-iron pipes over which water trickles from a perforated trough.

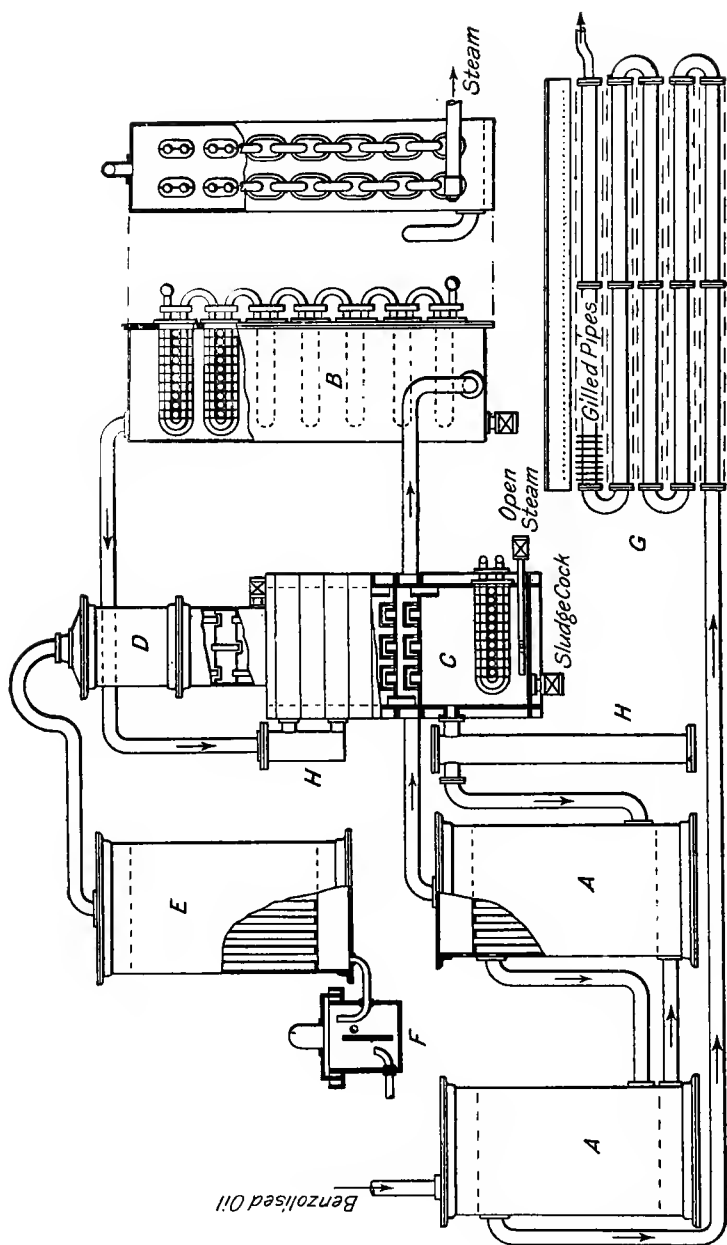


FIG. 31.—R. AND J. DEMPSTER'S DEBENZOLISING PLANT.

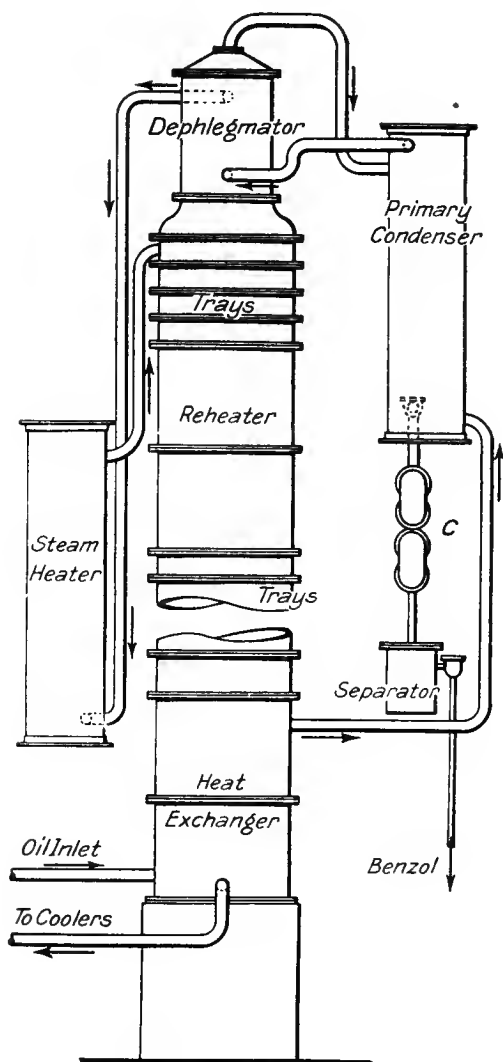


FIG. 32.—ARRANGEMENT OF SIMON CARVES' CRUDE BENZOL PLANT.

The Simon Carves' plant, the general arrangement of which is illustrated in FIG. 32, also presents some interesting peculiarities of design. After passing through the oil oil heat exchanger, the benzolised oil enters in turn the primary condenser (or vapour/oil

exchanger) dephlegmator, and steam heater. By this means it may be raised to  $140^{\circ}\text{C}$ . before entering the bubbling trays

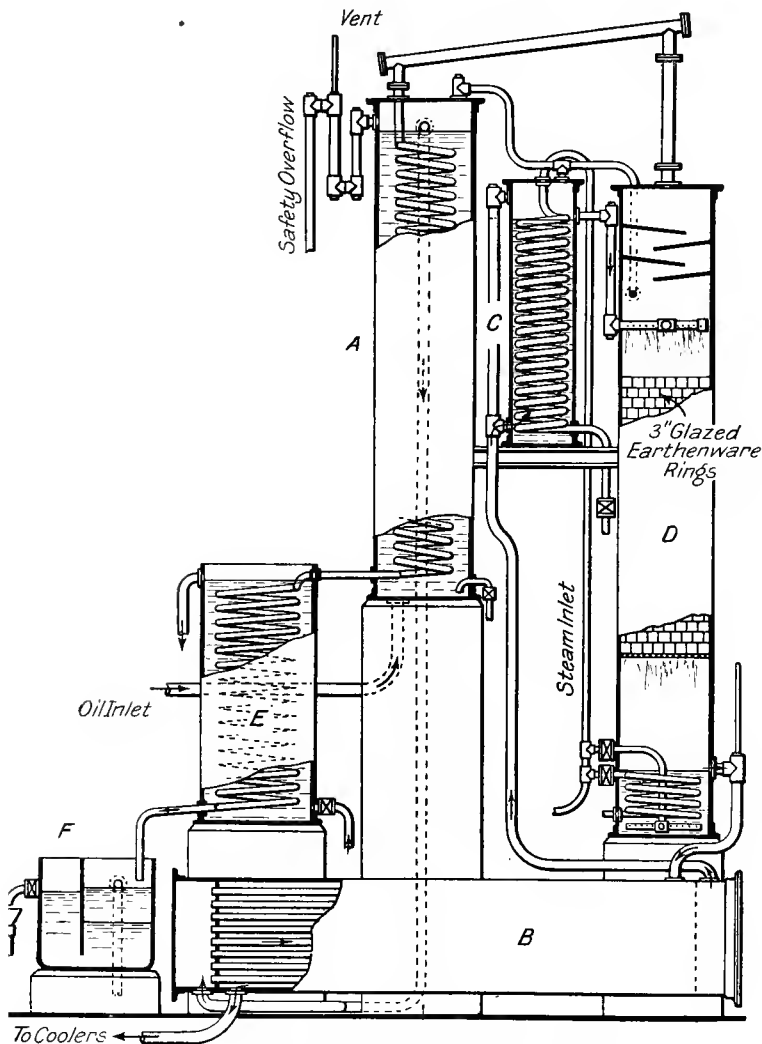


FIG. 33.—“ WANDSWORTH ” CRUDE BENZOL PLANT.

of the still. These trays are separated into two portions by a chamber called the “ reheater,” which contains a large cast-iron

steam coil. The evaporation of the distillates in the upper section of trays necessitates the abstraction of their latent heat from the oil, the latter being consequently reduced in temperature. The function of the reheater is to make up this deficiency, and as a result, the makers are enabled to guarantee not more than 0.5 per cent. of water in the debenzolised oil.

Another interesting feature of the plant is the annular benzol condenser (C, FIG. 32). This form of condenser to which reference has been made on p. 69, is exceedingly efficient and economical.

During the war many "home-made" benzol plants, of which the "Wandsworth" crude benzol plant is typical, were constructed from second-hand material. These were of various designs, most of which gave good results. One of the earliest and most satisfactory types of such plant was that devised by H. O. Carr, and his arrangement of the parts will be understood by reference to FIG. 33, which shows an installation constructed throughout in mild steel and wrought iron. A number of these plants were erected with all kinds of material that was available—including large cast-iron mains—and worked very well. In the arrangement shown the benzolised oil enters the shell of a primary vapour condenser A where it is warmed by the condensation of some of the vapours. From A the oil passes to an oil/oil heat interchanger B of tubular construction, and thence to the preheater C which contains one or more steam coils, whereby the oil is raised to the requisite temperature before entering the column still D. This is of simple construction, and is packed with earthenware rings 3 inches long  $\times$  3 inches in diameter, over which the hot oil is distributed from a perforated cross-pipe. The base of the column acts as a reservoir and contains a closed steam coil in addition to the open steam spray. The debenzolised oil flows *via* the heat exchanger to the oil coolers (not shown in FIG. 33), consisting of lengths of 3-inch wrought-iron piping sprayed with water. The upper portion of the still above the oil inlet is fitted with baffle plates to prevent priming, and all parts of the apparatus are provided with vent pipes, where necessary, and with vapour off-takes. The latter are connected into a common vapour pipe, through which the vapours are conveyed to the primary condenser A, and finally to a water-cooled condenser E and separator F.

### Direct-fired Plants

So long as the oil entering the still is maintained at  $120^{\circ}$ — $125^{\circ}$  C. the method by which it is raised to this temperature is of relatively small importance and therefore the heating may be performed by direct-firing equally as well as by steam. Where there is a shortage of steam as well as in cases where the steam supply is wet or at a low pressure, direct-fired debenzolising plants may be installed with success, and, in fact, some writers have expressed

a preference for this method of heating. The author's experience, however, indicates that whenever a plentiful supply of steam at not less than 70 lbs. per square inch pressure is available, steam-heated benzol plants are by far the more satisfactory and economical type. The outstanding difference in the working of the two kinds of plant is the fact that direct-firing entails more labour, in constant attention to the fire, whilst a plant heated with steam may be made practically automatic, and put in charge of a man doing a considerable amount of other work. There is also the risk of igniting the wash-oil or benzol, and more important, perhaps, is the greater consumption of wash-oil in the direct-fired plant.

There is always a certain amount of local overheating in such a plant, and this results in "cracking" and excessive thickening of the oil. For the same reason the heating elements are liable to become blocked with carbonaceous deposits, which act as very effective heat insulators in the most undesirable position; increased fuel consumption may result, together with the possibility of burning out or fracture. Nevertheless, direct-fired plants have done useful work in many cases, and they are to be preferred to steam-heated plants supplied with very wet or low-pressure steam. It should be added that even on this type of debenzolising plant, open steam is necessary for successful stripping of the oil.

Pot stills may, of course, be used intermittently for the purpose as in the distillation of tar. Owing to the large proportion of wash-oil to benzol, this is very wasteful and tedious. As a result, several firms have placed continuously operated pot-stills on the market for debenzolising wash-oil. It is not proposed to discuss these in detail, since they are unsatisfactory and undesirable. The large bulk of oil in the still is thermally wasteful, and intimate contact between it and the open steam introduced is a practical impossibility. It will suffice to say that a still 7 feet high and 5 feet 6 inches in diameter will deal with about 3,000 gallons of wash-oil per twenty-four hours, and that such stills are usually fitted with a short fractionating column refluxing into the still, as well as the usual heat exchanger, condenser, etc. J. Parker has described an ingenious alteration by which the efficiency of a pot-still was much improved. The still itself was used as a preheater, and this was worked in conjunction with a "Southport" column still (see FIG. 34).

The "Southport" plant was designed by the author's former chief, John Bond, of Southport, and during the war was applied with the greatest ease and success to many gasworks. The plant may be steam-heated, but was originally intended for direct firing to meet the case of the large number of gas undertakings having no spare boiler power. It was designed with a view to avoiding the defects enumerated above, and is shown in FIG. 34. Two cast-iron or steel pipes, 18 feet long  $\times$  16 inches







in diameter, are placed horizontally in a small setting and heated by the gases from a coke or breeze fire. The pipes are protected from overheating by a firebrick arch, and the gases from the furnace pass under this arch, finally around the pipes and away to a chimney. Oil passes continuously through these pipes in parallel, and is heated to  $120^{\circ}\text{C}$ . before entering the column still, which is the chief feature of the plant. It consists of a wrought-iron cylinder packed with iron rings and steel turnings. The oil enters at the middle of the column (which is, of course, well lagged) and is distributed over the packing in its lower half. In its descent the oil meets the ascending benzol vapours and live steam, which is introduced at the base.

Very intimate contact is thus assured by the scrubbing action of the packing, and remarkably thorough stripping of the oil results. The upper half of the cylinder serves, in a similar manner, as an efficient fractionating column, and the vapours leaving at the top represent a high quality of benzol. This is condensed in a compo. worm immersed in water, the condenser tank being constructed of wood and coated internally with tar.

A feature of the plant is the annular counter-current heat exchanger, the design of which is apparent from FIG. 34. A by-pass pipe, fitted with a large gland-cock, connects the heating tubes with the heat exchanger, so that, in the event of a fracture of the former, or any other mishap the heaters may be rapidly emptied.

By the use of a coil or other preheater in conjunction with the column, the "Southport" plant may be adapted for steam heating, and such an installation has been described by C. F. W. Rendle (*Gas World*, Jan. 12, 1918, p. 23).

### Debenzolising in Tar-dehydration Plants

Plant originally erected for the dehydration of tar has, in many cases, been successfully adapted for debenzolising wash-oil, and the makers of such plant can now offer a combined form of installation suitable for both purposes. A dehydrator is essentially a continuous direct-fired still, provided with heat-interchangers, condenser, etc., but usually with very little fractionating apparatus. The addition of the last will enable the plant to be used for producing an average quality of benzol, and if such an addition forms a by-pass to the existing arrangements, the plant may be put to its original use when desired. FIG. 35 shows, in diagram form, a fractionating column of the "Southport" design added thus to a dehydration plant of the "rectangular still" type. In this case the condensate is taken away for separation of naphthalene, as described later. A similar addition may be easily made to any dehydration plant.

The Hird-Chambers plant, as constructed by Messrs. W. C. Holmes, Ltd., is shown in FIG. 36, and in that form is suitable for tar dehydration (its original purpose) and debenzolising.

For the latter purpose an oil- or water-cooled dephlegmator has been added, and open steam jets are introduced beneath the surface of the oil, which is heated by means of steel flue tubes passing through it. The source of heat may be either a breeze furnace or gas burners in the ends of the flue tubes, and FIG. 36, which shows the former arrangement, is self-explanatory as regards the remainder of the plant. In conjunction with coke-oven plant, surplus gas provides a very economical fuel.

Wilton's dehydration plant comprises a long cast-iron coil in a brickwork setting heated by a coke fire. Tar is passed

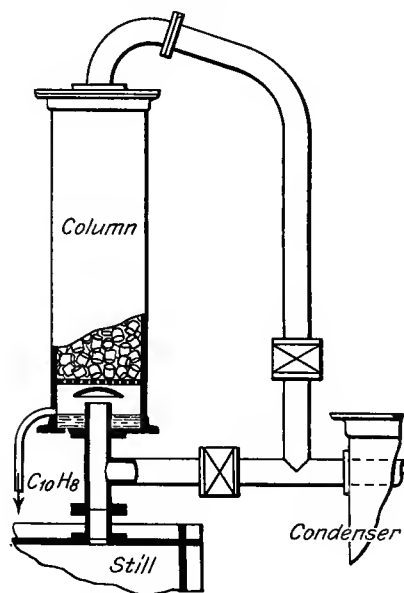


FIG. 35.—FRACTIONATING COLUMN ADDED TO DEHYDRATION PLANT.

upwards through this coil under a few pounds pressure, and when hot is suddenly released into a "vapour box" at atmospheric pressure. The light oil vapours are taken off to a condenser, and open steam is introduced into the vapour box which may be replaced for debenzolising by a fractionating column fitted on a by-pass. Alternatively the hot oil from the coil may be led into a bubbling tray still as in the ordinary steam-heated plant, and this constitutes a very satisfactory form of direct-fired apparatus.

If a dehydration plant is to be used for both purposes oil coolers must be added, and a separate heat-exchanger should also be installed. If the same be used alternately for both tar and wash-oil, contamination and thickening of the oil will result.

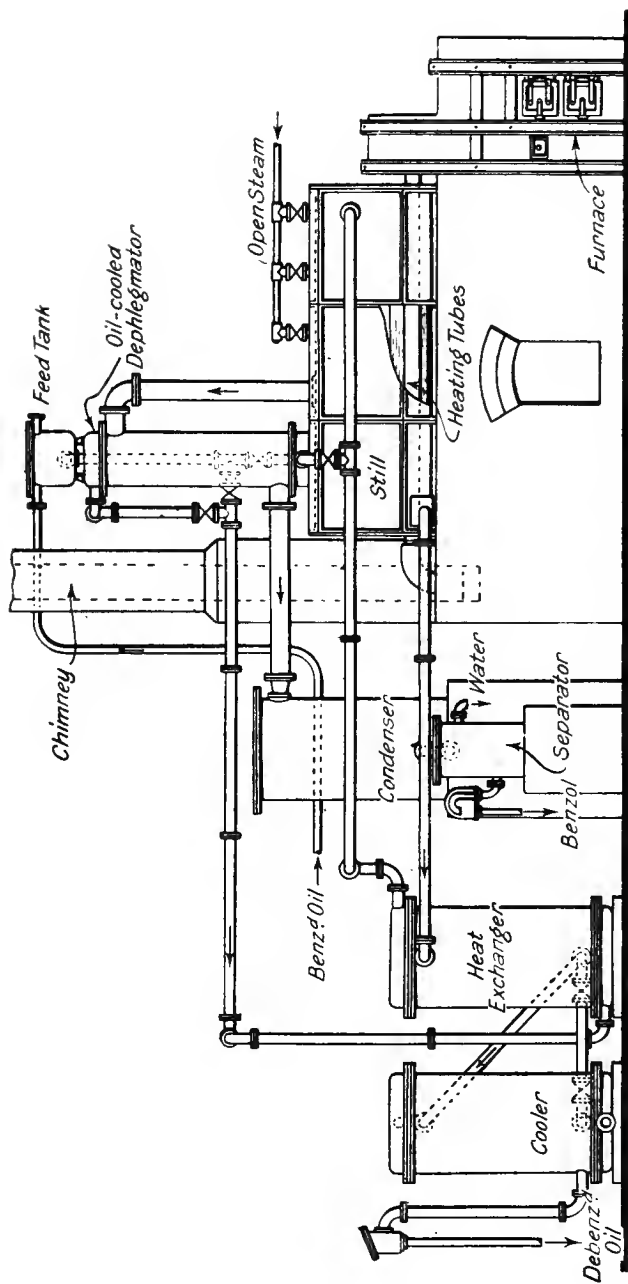


FIG. 36.—"HIRD" (W. C. Holmes, Ltd.) COMBINED PLANT FOR DEBENZOLISING AND TAR-DEHYDRATION.

## CHAPTER V

### ACCESSORY PLANT

HAVING considered the essential portions of the debenzolising plant attention may be given to the subsidiary apparatus.

#### Oil Feed Arrangements

One of the first essentials to the successful and automatic operation of a crude benzol plant is a means for ensuring regularity in the supply of benzolised oil, and the writer's experience has invariably proved that a direct pump feed is on the whole unsatisfactory. Even under the best conditions—a fly-wheel pump, for instance, supplied with steam through a reducing valve—troubles occur from time to time which vary the flow of oil, and, in consequence, interfere with the thermal equilibrium and smooth working of the still. This difficulty is much intensified when the plant is fed by a direct-acting, or wheel-less, pump. Any slip in the cylinder can only be counteracted by adjustment of the steam valve; and there is no margin whatever for dealing with a rush of oil, or any slackening in its flow brought about by a variation in boiler pressure. This is particularly evident in a gasworks of medium size, where the load on the boilers varies very considerably, together with irregular firing and clinkering.

Undoubtedly the best arrangement is a constant-head feed, the oil passing through a regulating valve under constant pressure. This may be attained in two ways: either by the use of an overhead tank fitted with inlet, outlet and overflow pipes, or by the erection of an inverted U pipe.

The former arrangement, though the more costly, is probably the better, since the pump may then be stopped for a short period (depending upon the capacity of the tank) whilst glands are re-packed or valves renewed, without seriously affecting the passage of oil to the plant. In the second case the delivery pipe from the pump is taken up some 8 or 12 feet above the maximum height of the oil level and then, bending over, returns to the benzolised oil tank. The top of the bend is provided with a vent pipe to prevent siphoning, and the oil inlet pipe to the plant is taken off at a point between the pump and the bend. The two arrangements are shown in FIG. 37, in which P is the pump, R the regulating valve, O the overflow pipe, E the inlet to the heat exchangers, and H the constant head. In use, the pump

is run at such a speed as will give always a small overflow from the tank (or past the bend) the fixed position of which gives the constant head.

It is advisable to fix the regulating valve (of the ordinary disc type, or preferably J. E. Grainger's patent valve) on a hori-

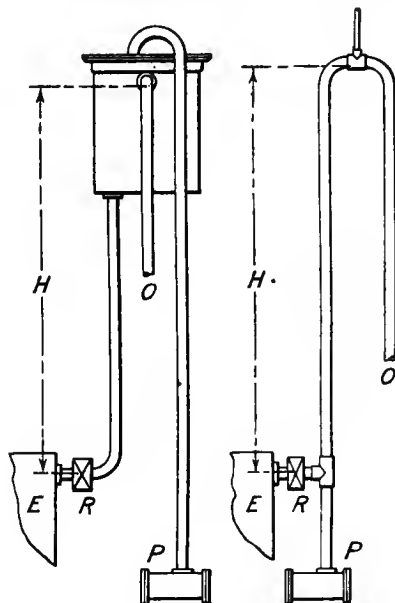


FIG. 37.—CONSTANT HEAD OIL FEEDS.

zontal portion of the pipe, since its being placed vertically renders it liable to stoppage by particles of dirt, anthracene, etc., in the oil. As an alternative to a valve the oil flow may be regulated by a jet or orifice of a suitable size. Whilst this arrangement is satisfactory for a fairly constant make of gas, it is obviously less flexible than the use of a valve.

### Storage Tanks

Little need be said under this heading since the use of old boiler shells, after cutting out the flues and blanking off the ends, is the cheapest and most satisfactory method of storing oil. In the case of plant erected during the war it was not always possible to find boiler shells for this purpose, and other forms of storage were adopted in some works, old cast-iron tanks being in many cases purchased and re-erected; it was then, of course, necessary to pay great attention to the jointing in this work, owing to the

great ease with which tar-oils, benzol, etc., penetrate the slightest imperfection in the joint, the complete ruin of which very soon follows.

During the war interesting substitutes for metal tanks were wells constructed either in concrete or in cement-rendered brickwork. One such tank has been in constant use for two years and has given no trouble whatever. It is in the form of a rectangular brickwork tank, well rendered with hydraulic cement, the top—on ground level—being constructed in concrete reinforced with old rails and tee bars. It is found best to apply a fairly heavy cement rendering, whether the tank be of brick or concrete, and it has been thought that in one or two cases constituents of the creosote have acted chemically upon the cement, causing porosity and, in time, leakage. Experiments show, however, that this difficulty may be easily overcome by coating the surface of the tank with a solution of water-glass. This has been tried with several tanks and has proved successful in each case.

Provision should be made for storing a reasonably large quantity of both benzolised and debenzolised oil, in order that the distillation plant may be kept running during repairs to the scrubber and *vice versa*. As a rough guide, a works carbonising 100 tons of coal per diem should have wash-oil tanks of a total capacity of at least 5,000 gallons. The larger of two tanks should be used for debenzolised oil, since this arrangement offers more opportunity for any entangled water to separate out and also for the oil to cool down in the event of any temporary inefficiency of the coolers. This has been found of use in hot summer weather. For a small works, one boiler tank may be installed and divided into two chambers by a riveted division plate, or even by a 9-inch wall of bricks set in cement. Slight leakage through the division is not of very serious moment.

Wash-oil tanks should be fitted with sludge-cocks of large diameter—2 inch at least—at their lowest points, in order that thick oil may be drained away. The pump suction should be not less than 6 inches from the bottom, and in large works it is advisable to arrange for the sludge-cocks to be rapidly connected up to one of the oil pumps for clearing purposes. In addition to the usual man-lid, inlet and suction pipes, a float may with advantage be fitted to each oil tank, so that the oil level may be roughly found at a glance. Both tanks should be protected from the sun if possible, and rain must not, of course, be allowed to enter. The benzolised oil tank should be kept sealed, with the exception of a small vent pipe, to prevent evaporation of the benzol; but the delivery to the debenzolised creosote storage should be made through a "tun-dish" or other sight-feed arrangement, where the flow of oil through the system may be inspected and occasionally measured. If a weir be used (as shown in FIG. 13, p. 51) this is not necessary.

In small works the benzol is run direct from the separator into

the drums in which it is sold. On a larger plant, however, it is much more economical to despatch the spirit by tank wagon, and a benzol storage tank is then required. For this, also, there is nothing better than an old—but sound—boiler shell, and its capacity should be considerably greater than that of a tank wagon, in order to obviate the shutting down of the plant through delay to a rail-tank. Two wagon-loads, or about 5,000 gallons, is a convenient size of tank for a gasworks. If the crude spirit is rectified on the producer's works, the necessary storage will, of course, entirely depend upon the arrangements made for this process.

Benzol tanks should be protected from the sun, or, if this be impracticable, whitewashed or painted a light colour. They should be sealed, with the exception of a vent pipe, and if desired this may be a water-cooled worm of small compo pipe, forming a "reflux condenser." It has been suggested that a benzol tank is a source of danger in that it contains a mixture of hydrocarbon vapours and air which might explode on a light being brought near. This is a rather remote possibility, but it is perhaps safest to protect the vent-pipe with a cap or cowl containing two or three layers of fine wire gauze. Alternatively the tank may be filled with gas and the vent-pipe connected up to a neighbouring gas pipe—if the latter be before the oil scrubber, loss by evaporation is avoided.

The transportation of crude benzol in gasworks (*e.g.*, the loading of tank-wagons) is usually effected by pumping, since difference in levels rarely allows of loading by gravity. Moreover, benzol tanks of any capacity should never be supported high above ground level, on piers or columns, in view of the disastrous results of a fractured cock or connection. By far the better method is that of the tar-works, where such liquids are commonly "blown" from tank to tank by compressed air. Many gas undertakings already have air compressors for operating the stoking machinery; even if this be non-existent, a works of any size would be well advised to instal a small compressor for this work, since it offers a safer, cleaner and more rapid method of handling the spirit. In this case a means of completely sealing the tank is necessary, and a cock must be provided on the vent pipe. A pressure gauge is desirable, and care must be taken to fit a good sound cock on the pipe leading the benzol from the tank. Otherwise the large volume of compressed air remaining will, sooner or later, cause a tank-wagon to be filled to overflowing. A space of several inches should be left between the bottom of the tank and the benzol exit pipe, whether this be a pump suction or pressure delivery, in order that traces of water may settle out. In all cases it is important that a water-cock be fitted at the lowest point, and on this account a benzol tank should have a few inches fall to one end.

Tanks for both wash-oil and benzol are frequently placed in

pits below ground level. It is usually necessary to sink them in the ground in order to obtain sufficient fall in the pipes, and a brick or concrete pit undoubtedly makes a better and safer job. There is also the advantage that any leakage is very soon detected, the tanks being raised on low piers.

### Pumps

It has been stated that a benzol recovery plant may sometimes be so arranged that only one pump is required for oil. Usually two are necessary, and also sometimes one for benzol, whilst the necessity for a water-pump will depend upon conditions and source of the supply. For reasons explained above, fly-wheel pumps should invariably be preferred to the direct-acting type, and for oil, benzol or tar, the author knows none better than Messrs. Joseph Evans' reversible pump. This is made in a large range of sizes, and is of the ordinary fly-wheel and piston type. The sheave of the eccentric is secured to the crankshaft by a set-screw. By loosening this screw and turning the sheave through a small angle, the action of the pump may be reversed; this is often very useful in cases of blocked suction pipes and in some emergencies, such as a fracture on a direct-fired plant. Centrifugal pumps are sometimes used, and J. A. Wilson states that they are quite satisfactory, if designed with sufficient length of gland to take three laps of  $\frac{3}{8}$ -inch packing.

The whole of the pump must be constructed in iron, including the valves. Pump valves of rubber or similar composition are obviously inadmissible, whilst those of brass or gun-metal rapidly corrode. A pump should be chosen with facilities for rapidly exposing and cleaning the valves and their seatings, owing to the liability for deposits to form here and cause trouble.

Creosote, especially when benzolised, is best pumped under pressure, and pumps for this purpose should be situated as near as possible to the lowest point of the pipe line, both on this account and to obviate the necessity for frequently priming the cylinder—a somewhat uncomfortable operation with tar-oil.

### Connections

It has been stated previously that pipe connections should be of ample size, and that nothing less than 2 inch diameter should be used except for very small works. For those carbonising 20 tons of coal per twenty-four hours this size is suitable, and the pipes vary from this to, say, 4 inches for an amount of gas corresponding to 400 ton sper diem. Bends should be used throughout in preference to elbows, and vent pipes fitted wherever there is a likelihood of air- or vapour-locks. When a pipe is intended to convey hot benzolised oil, provision should be made for the passage of this as foam, and a correspondingly larger pipe put



in. If it is necessary to carry an oil pipe down in U form it is advisable to leave caps or plugs on the ends of the lowest portion to facilitate cleaning out, and one of these plugs may be conveniently replaced by a cock for emptying. This is indicated in

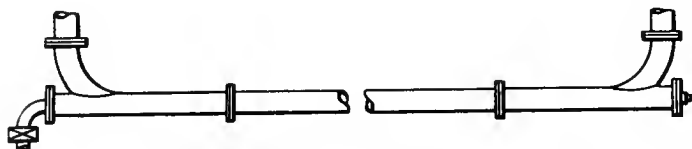


FIG. 38.—ARRANGEMENT FOR CLEARING PIPES.

FIG. 38, and the Y pieces there shown should be used in preference to tees. By-pass connections are often useful, and should always be added to the oil coolers, as explained on p. 73. A return connection should also be put in from the outlet of the coolers to the benzolised oil tank, in order to avoid the passage of benzo-

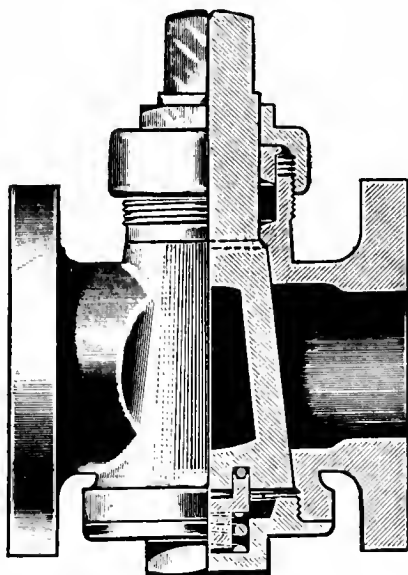


FIG. 39.—BUTTERFIELD COCK.

lised oil into the debenzolised storage when starting up, and before the plant is sufficiently hot for the use of live steam. A by-pass to a pump which is somewhat too big for its work is never satisfactory; if a constant-head feed is adopted, however, it is unnecessary.

## Cocks and Valves

Ordinary plug cocks are seldom satisfactory for creosote and similar oils, and when the oil is hot will hardly ever prove suitable. A good type of gland cock is much to be preferred and, of course, must be of cast-iron. Periodical attention to the packing of the glands is necessary. A very good form of gland cock, especially in the larger sizes, is that designed by Butterfield, which is a full-way cock and in which tightening of the gland causes the plug to be pulled up to its seating owing to the reversed taper of

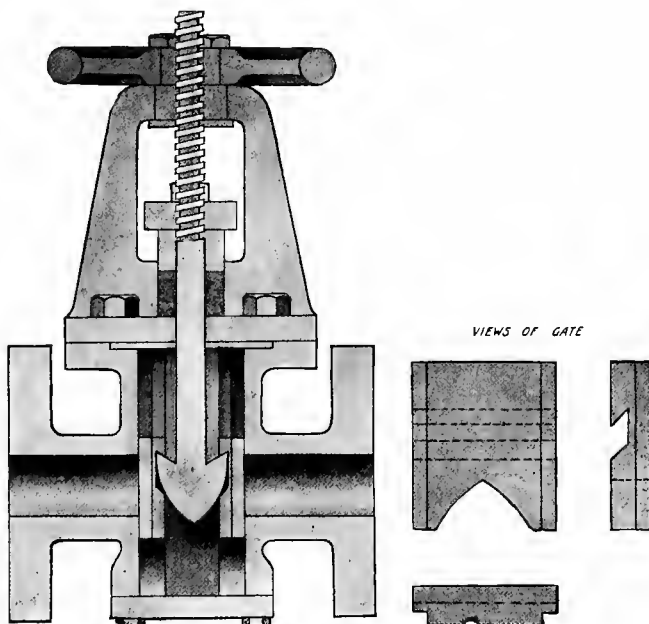


FIG. 40A.—GRAINGER'S PATENT GATE-VALVE.

the former. The construction of this cock is shown in FIG. 39. Ordinary plug cocks are suitable for benzol and water, but should be of cast-iron. Gun-metal cocks rapidly corrode, particularly those in contact with separator water.

Valves for steam need no description here, and for wash-oil valves are rarely necessary except for regulating the flow of oil to the plant, and, on the larger works, for isolating various tanks and on by-pass connections. They should be of cast-iron of the usual "gate" or "disc" type, and should be fixed vertically upright, *i.e.*, so that, when the valve is partly open, the orifice

is always at the bottom of the pipe. This minimises the possibility of blockage by solid matter.

For the regulation of oil-flow, and, indeed, for many other purposes, the valve patented by J. E. Grainger and made by Haughton's Patent Metallic Co., is most useful. This valve, illustrated in FIG. 40, is essentially a substantially built sluice valve, with external bolts and other evidences of the application of experience to its design. It differs from the ordinary type



FIG. 40B.—GRAINGER'S PATENT GATE-VALVE.

of valve in having a V-notch in the bottom edge of the sliding gate. The usual gate-valve, when only slightly opened, presents a long and very narrow "new-moon" orifice. This renders the regulation of small flows difficult if not impossible, and also creates a tendency for any solid particles to accumulate and block the passage. The great superiority of the new valve is apparent, for whilst the fully open portion gives a full-bore passage, regulation of a smaller flow is effected by raising or lowering the apex of a triangular orifice—a very sensitive arrangement, and one in which the possibilities of a blockage are reduced to a minimum. The valve gives good results with oil, benzol, water and steam, and is made in both cast-iron and gun-metal.

Safety-valves set to blow at, say, 8 lb. per square inch should always be fitted to direct-fired stills, and it is perhaps safer to add them to the preheaters and stills of steam-heated plants. A suitable connection is put in for taking off any escaping oil from the former.

### Steam Supply and Regulation

Although the necessity for a supply of dry steam at as high a pressure as possible has been emphasised in the preceding chapter, it is as well to again draw attention here to the necessity for lagging all steam pipes. It is well known that the saving in heat alone more than repays the cost of insulating the pipes; in a benzol plant one is confronted with the added evil of water in oil as a probable result of wet steam. If the boilers are worked at a fairly high pressure—say 90-100 lb. per square inch—it is advisable to add a reducing valve to the main supply, and by

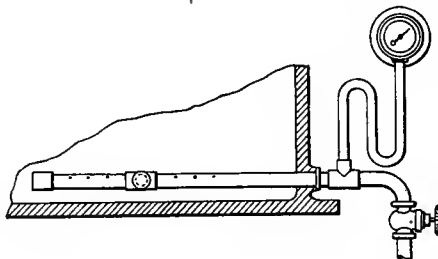


FIG. 41.—REGULATION OF OPEN STEAM.

this means to reduce the pressure to, say, 80 lb., at which it will remain constant irrespective of fluctuations at the boiler. Such an arrangement is a great help towards automatic running of the plant and consequent saving in labour costs.

The steam supply to the preheaters, and to the dry steam coil (if any) in the still, should be regulated by valves or steam-traps at the respective outlets in preference to the inlets; in this way full pressure is maintained in the coils, etc., and a higher duty obtained. The regulation of the open steam entering the still always presents some difficulty owing to the relatively small valve opening required to pass it. Thus for 100 tons of coal per diem, sufficient open steam will pass a half-inch valve when opened to the extent of only one quarter of a "turn." This state of affairs naturally causes scoring and erosion of the valve surfaces, with consequent detriment to the regulation. To overcome this, some makers of plant reduce the open steam to 5 or 10 lb. pressure before regulation, but this can hardly be called a satisfactory solution. Wet steam is partially or, some-

times, completely dried by expansion ; dry steam under similar treatment becomes slightly superheated. In order, therefore, to take advantage of this effect the reduction in pressure should be performed by throttling as near to the still as possible. As the result of experience the author considers the arrangement shown in FIG. 41 to be the best. A " spray " or distributor having a limited number of small holes is used in the still, near to which the steam pressure is regulated by means of a valve. The jets of the distributor are sufficient in number and size to pass the requisite quantity of steam at a moderately low pressure, say 10 lbs. per square inch. A sensitive gauge is fitted between the valve and the still, and its indications serve to show roughly the amount of steam passing. With the supply arranged in this way scoring of the valve is of no moment, and enlargement of the distributing orifices is reduced to a minimum by the preceding reduction in pressure. The reading of the gauge, and the flow of water from the separator, provide all the " metering " of live steam required.

If the steam supply to the plant is unavoidably wet, due to long travel, etc., superheating may be resorted to with advantage. In the case of a direct-fired plant, the steam introduced into the still may be readily dried by passage through a few turns of piping situated in one of the flues. If the plant be steam-heated, the whole of the steam should be passed through a separator, and finally through one of the numerous superheaters on the market ; this may be heated by gas or by a coke- or breeze-fire.

### Thermometers and Gauges

It is absolutely necessary to have reliable thermometers at various points on the debenzolising plant, and these are best fitted in mercury cups, as shown at A, FIG. 42. A wrought-iron or steel thimble is screwed into the pipe and partially filled with mercury, in which the bulb of the thermometer is immersed, the latter being of the usual chemical type, and fitted into the thimble by means of a cork. If a cased thermometer be preferred the mercury cup is not necessary, the bulb of the thermometer being enclosed in a perforated tube, and leakage being prevented by the joint made between the stem and the outer case (*see* B, FIG. 42). A dial thermometer, as is often used in gas mains, is also a very good form for certain positions. All thermometers should be checked at about their normal working temperature before use.

The most important temperature on a debenzolising plant is that of the oil leaving the still, and accordingly a thermometer must be provided either in the lowest chamber of the still or in the debenzolised oil pipe immediately after it. Other essential thermometers are those at the outlet of the preheaters, and in both gas and oil entering the scrubbers. Thermometers should also be fitted between the heat exchangers and preheaters, and

in the oil leaving the coolers, whilst it is often desirable to know also the temperature of the vapours leaving the still-head. If a separate dephlegmator is used for elimination of naphthalene, the temperature of the vapours leaving this piece of apparatus is essential to proper control.

In the case of a thermometer used for taking the temperature of oil in a partly filled pipe, every effort must be made to ensure the actual immersion of its bulb (or mercury cup) in the oil itself. Much trouble has been caused by thermometers reading incorrectly from this cause, which may be overcome by arranging

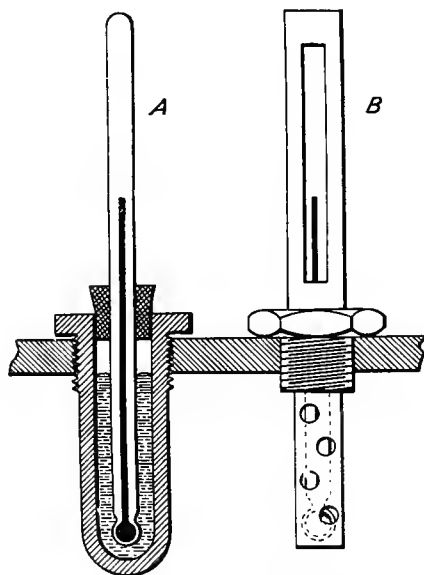


FIG. 42.—FITTING OF THERMOMETERS.

a rise in the pipe after the thermometer, or by fitting a small weir or baffle. For similar reasons, a thermometer should never be inserted to such a distance that its bulb is in contact with the opposite surface of the pipe.

Steam gauges are necessary, and their application is too obvious to need description. It is usual to add a glass tube gauge to the base of the still in order to indicate the oil level and, consequently, any back pressure in heat exchangers or coolers. In the case of a direct-fired pot-still such a gauge is certainly advisable, but should be fitted on the side of the still remote from the firing door in case of fracture. These gauge tubes should be protected by a metal sheath and, of course, fitted with cocks at both ends.

An automatic separator requires no gauge; the levels of the liquids it contains may be checked occasionally by slowly immersing a glass tube in the distillate and withdrawing it, after the manner of a pipette, with the finger closing its upper end. If the separator be not automatic it is necessary to have a gauge to show the line of separation of benzol and water, and the upper gauge cock must therefore be below the surface of the benzol.

### Meters and Sight-feeds

The flow of wash-oil may be conveniently measured by a V-notch as described on p. 51 and in FIG. 13, and also by several meters which are on the market. One of these is an inferential meter; the oil passes over a plate in which are five equal circular holes, and the oil passing through one of these is measured, five times its volume being recorded. Such meters, whether used for wash-oil or for benzol, should contain no brass or copper internally. As regards measuring or indicating the rate of flow of benzol from the plant, the writer prefers a simple swan-neck sight-feed; the approximate rate of flow can soon be judged after a little practice, and in any case periodical dipping of the benzol storage tank is advisable. Some makers equip their plant with sight-feed arrangements having some means of indicating the flow, and one form consists of an elbow on the benzol delivery pipe into which is screwed a vertical length of pipe. This pipe is drilled with small holes at intervals, and the volume of the benzol stream is indicated by the number of holes required to pass it, each hole corresponding to a certain number of gallons per hour. Such devices can hardly be looked upon as accurate, and, when fitted at the outlet of a non-automatic separator, are practically useless.

### Sampling

A device for sampling the benzol made is illustrated in FIG. 27, p. 71. Means must also be provided for obtaining representative samples of oil entering and leaving the system, *i.e.*, of benzolised oil entering the heat exchangers and of debenzolised oil leaving the coolers. Samples of debenzolised oil entering and leaving the heat exchangers should also be taken occasionally in order to detect short-circuiting in that piece of apparatus.

## CHAPTER VI

### OPERATION AND CONTROL OF THE APPARATUS

THE method employed for debenzolising the saturated wash-oil depends upon the type of plant. The remarks immediately following refer to the usual continuously working steam-heated type, while direct-fired plants will be referred to later. In these cases the process is continuous, and is therefore much simpler and more economical, as well as entailing less plant and labour, than the intermittent distillation of the oil in a pot-still. Intermittent distillation is fully explained in A. R. Warne's valuable book *Coal Tar Distillation*; but as it is never to be recommended for debenzolising no further attention will be given to it here.

#### General Operation

The operation of a steam-heated debenzolising plant is in itself comparatively simple. There are, however, a few points to which very careful attention must be paid, and the neglect of one or more of which is sufficient to turn successful running into a complete failure and source of expense. We have seen that the "golden rule" for the scrubbing process is: "Keep the temperature of the wash-oil about  $2^{\circ}$  C. higher than that of the gas." Similarly, there are two rules to be observed on the debenzolising plant:—

- (1) Always keep the oil leaving the still above  $100^{\circ}$  C.
- (2) Pay careful attention to the open steam supply.

It may be said at the outset that the average steam-heated plant will work satisfactorily when the oil leaving the preheaters, and entering the still, is at  $120^{\circ}$  C.; and when such a quantity of open steam is used as will give a distillate consisting half of benzol and half of water. This is a rough guide, and will necessarily vary with the saturation and water content of the oil, the amount of fractionation and other factors. Such conditions will result in the debenzolised oil leaving the still at about  $105^{\circ}$  C., but this figure will be somewhat higher if a closed steam coil is used in the base chamber, and will also vary with the dryness of the open steam and the saturation of the oil. The drop in temperature from inlet to outlet of the still represents the sum of the latent heat of evaporation of the products, plus the heat losses through radiation, etc., less the extra heat added as open steam.



### Tests on Oil and Benzol

The working of the plant must be under capable chemical control and tests must be performed regularly on benzolised and debenzolised oil, and on the crude benzol. Tests on the oil have been fully described in Chapter III. (pp. 56, 57). When the plant is working satisfactorily the debenzolised oil should contain not more than 0.5 per cent. of water, and the refractionation of the oily distillate should give not more than 0.5 per cent. of the original oil at  $120^{\circ}\text{C}$ . (or not more than 0.8 per cent. at  $160^{\circ}\text{C}$ .). The usual test for benzol is the "retort test," in which 100 c.c. are distilled in an 8-oz. retort to  $120^{\circ}\text{C}$ ., the bulb of the thermometer being immersed in the liquid, and  $\frac{3}{8}$  inch from the bottom of the retort. This method of testing cannot be too strongly condemned. It is unscientific in principle and, though perhaps comparative for one particular plant, is quite untrustworthy in its results. A far better test is that devised by the Department of Explosives Supply in connection with its benzol bonus scheme. In this test 200 c.c. of the spirit are distilled from a round bottomed flask through a 12-pear Young's fractionating column. The speed of distillation is regulated to one drop per second, and the bulb of the thermometer is fixed slightly below the vapour outlet of the column. A "normal" crude benzol is defined as one giving 80 per cent. of distillate at  $120^{\circ}\text{C}$ . by this test, and experience indicates that this is the most economical standard to work to in most cases. Such a product would usually give 65 per cent. at  $120^{\circ}\text{C}$ . by the retort test.

### Sampling

Spot samples give very little information as to the working of the plant. The method of sampling advised by the author necessitates three 2-gallon cans. Samples are taken by the attendant every hour, or two hours, of benzolised and debenzolised oil and of benzol. Each morning the contents of the cans are shaken up and the corresponding tests performed. Any defect is further investigated by suitable "spot" samples.

### Starting-up the Plant

On commencing benzol recovery, wash-oil is passed through the washer until sufficient benzolised oil is in stock to fill the debenzolising plant and to give a margin of oil to work with. The washing process should be started slowly, with, say, only 10 gallons of oil per ton of coal, and this figure increased gradually to the desired volume over a period of a few days. In this way the effect on the gas may be studied, and an abrupt alteration at the consumer's burner is avoided.

On p. 89 the addition of a by-pass connection from the outlet of the coolers to the benzolised oil tank was advised. If this has been put in, starting up the plant is a very simple operation. Benzolised oil is pumped, *via* the constant head feed tank, through the plant, and back through this by-pass to the same tank, the rate of flow being that normally expected. Water is supplied to the coolers and steam to the preheaters and to the closed steam coil (if any) in the still. One important rule must always be observed, viz. : *Do not introduce open steam until the temperature of the oil leaving the preheaters is well over 100° C.* On reaching a temperature of, say, 105° C. at this point, open steam may be gradually introduced. At the same time a watch must be kept on the temperature of the oil leaving the still. Should this be below 100° C. the use of open steam must be postponed. When the oil leaving the preheaters is about 95° C. some benzol will probably distil over ; this will be of high quality, and will represent only the lighter portions of that in the benzolised oil. The oil leaving the system is, therefore, only partially stripped, and the use of the by-pass connection is desirable, in order to avoid the return of this oil to the scrubbers.

If no by-pass connection exists the plant must be filled with oil and the supply of the latter then shut off. Closed steam is admitted at full pressure until the oil in the plant is thoroughly heated, when the flow is restarted from the overhead tank or pump. If the temperature of the oil is below 105° C. the oil must be again shut off and the process repeated, taking the same precautions with regard to the introduction of open steam.

On attaining a temperature of 120° C. at the outlet of the preheaters (and 105°—110° C. at the outlet of the still) the open steam is adjusted to give a " half and half " distillate, and the cooled oil may then be diverted to the debenzolised oil tank. Exact conditions as to temperature, etc., vary with the construction of the plant, so that a series of tests should be immediately instituted, and suitable adjustments made until these give satisfactory results. Consideration of theory will show that a higher temperature and an increased amount of open steam both tend towards a lower quality of crude, as well as to an improved stripping of the oil, and *vice versa*.

The working of the heat exchangers sometimes presents difficulty. It is evident that this portion of the apparatus cannot become fully effective until the ingoing debenzolised oil has reached its highest temperature. On the other hand, this temperature can rarely be attained without the assistance of the heat exchangers. Occasionally, therefore, it appears impossible for the plant to deal with the required volume of oil. Such conditions are best dealt with by allowing the oil to run full-bore through the apparatus for a time, and some hours may elapse before thermal equilibrium is reached.

### Normal Working

When the plant is in normal operation the chief points to be kept in mind are the temperature of oil leaving the still and the proportion of water to crude benzol in the distillate. These form sufficient data for most purposes, after a little practice and the performance of complete series of tests. But it is obvious that other observations should be made regularly and recorded in order that the working of every portion of the plant may be kept under control. A ruled book should be provided for the benzol attendant to record his observations, and a suitable form is shown in *Table 19*. This table also gives usual average readings; A, when an oil/oil heat exchanger is used; B, with a vapour/oil heat exchanger only; and C, with both types of interchanger in use. It must be remembered, however, that these temperatures are entirely dependent on the design, available surface, etc., of the apparatus.

TABLE 19.—TEMPERATURES, ETC., ON CRUDE BENZOL PLANT.

—	Hour.	Oil-flow. Galls. per hour.	Steam pres- sure, Lbs.	TEMPERATURES, ° C.							Water in 500 c.c. dis- tillate.
				Inlet to washer.		Outlet heat exchangers.		Outlet pre- heater.	Outlet still.	Outlet coolers.	
				Gas.	Oil.	Vapour oil.	Oil/oil.				
A.	—	—	100	15	17	—	65	120	105	17	250
B.	—	—	100	15	17	55	—	120	105	17	250
C.	—	—	100	15	17	50	80	120	105	17	250

If an analyser or dephlegmator is in use, as described in the following chapter, for the elimination of naphthalene, the temperature of the vapour leaving it must be observed and included in the above table—it will usually be about 93° C.—whilst even without this the temperature of the vapours leaving the still, about 95°–97° C., may be included if desired. It is advisable that these data be inspected each morning by the chemist in charge of the plant, and their averages should be entered by him in another book together with details of all tests, dippings of tanks, and particulars of benzol sold. It is also an advantage to draw up a sheet of instructions and to hang this, together with a diagram of the plant (showing all valves), in the benzol-house or pump-shed. The importance of regular chemical testing and the method of sampling have already been emphasised.

Every effort should be made to render the working of the plant

as automatic as possible by the adoption of steam-regulating valves, constant-head oil feeds, automatic separators, pump lubricators, etc. If these arrangements are attended to there is no need for the use of thermostats, as has been suggested at times. If intermediate tanks of small capacity are used, between two scrubbers working in series, for example, it is an easy matter to construct an alarm, comprising a float and suitable contacts to operate an electric bell in the event of the level of oil in the tank becoming too high or too low.

Storage tanks for both oil and benzol should be dipped regularly, in the latter case to ascertain the quantity made, and in the former to detect any leakage or wastage. In this connection a great saving of time may be effected by constructing a chart for each tank. This should be drawn to a large scale and may be plotted easily with the aid of the table in APPENDIX B. (p. 202).

The amount of oil entering the scrubbing system (or the debenzolising plant if preferred) is regulated and measured by a weir or any other method, and the same rate of flow is maintained through the other half of the plant by keeping the level of oil in one of the oil tanks (and therefore in both of them) approximately constant. Floats in the tanks are very useful in this connection.

The quality of the benzol made should not vary much provided other factors, and particularly the degree of stripping of the oil and gas, are constant, but it is advisable to mention here the effect of poor stripping. This has been considered from the theoretical point of view in Chapter II. (p. 29). The first effect, in practice, of incompletely debenzolising the wash-oil will be the production of a higher quality of crude owing to some of the higher benzenoid compounds remaining in the oil. We have seen, however, that a poorly stripped oil is not so efficient for the absorption of benzene, and therefore the quality will soon deteriorate, and will in time drop to considerably below normal owing to the lower absorption of benzene in the scrubber, and to the distillation of a greater proportion of toluol and solvent naphtha than exists in the gas. The oil will, then, in time contain a high percentage of solvent naphtha and results will fall off. The only way of dealing with such a condition is to resort to drastic stripping, and this entails the production of a benzol of very low quality for a time. In one such instance in the writer's experience, he was called to investigate the reasons for a falling off in the rate of recovery, and found no less than 8 per cent. of solvent naphtha in the wash-oil. The effect of increasing the open steam was a reduction in the quality of the product from 62 per cent. to 39 per cent. at 120° C. As soon as the oil became properly stripped, however, the results quickly reverted to the normal, both in quantity and quality of benzol recovered.

### Shutting Down the Plant

This presents little difficulty, the only point of importance being the necessity of closing the live steam valve first. Closed steam, oil, and, lastly, cooling water may then be shut off. If desired to cool the plant rapidly for repairs to joints, etc., oil may be kept circulating and returned, *via* the special by-pass, to the benzolised oil tank after the live steam supply is turned off. In this case, of course, water should be left running on the coolers. If the stoppage be only a temporary one, for renewing a joint, for example, the plant should be worked a little faster than usual for some time before the stoppage, in order to transfer as much oil as possible to the debenzolised oil tank, and so avoid a cessation of the scrubbing process. The reverse should be the case when scrubber repairs are contemplated.

### Operation of Direct-fired Plants

The same rules apply in the case of these plants as in steam-heated installations, but the control and regular working of the former is certainly more difficult. This is due to the irregular character of the heating—the need for periodically replenishing the fuel bed and clinkering the fire. Overheating must at all costs be avoided, but judicious use of damper and air-slides, combined with regular and frequent firing and clinkering, will in most cases suffice. Where this is not the case—and this has happened in not a few instances, particularly where the still is insufficiently protected from the fire—an approximately constant temperature can only be maintained by continual variation of the oil-flow. The quantity of open steam admitted must then be varied accordingly, and either the arrangement shown in FIG. 41 (p. 92) or a quadrant and pointer fitted to the wheel of the valve becomes necessary. Owing to these fluctuations, and in many cases to the design of the plant, the quality of benzol produced by direct fire is usually considerably less than that of benzol distilled by steam heat, and in consequence the wash-oil thickens more quickly. This is not the case, however, with the "Southport" plant which provides efficient fractionation, and in which the heating tubes are protected by a curtain arch.

As regards starting up a direct-fired plant much the same procedure is followed, and great care must be exercised to exclude open steam until the oil is sufficiently hot to prevent condensation. It is certainly easier to free the oil from water, emulsified or otherwise, by direct heat, but the quality of the oil suffers considerably in the process. But it is in shutting down that we find the principal difference in the operation of the two types. Most direct-fired plants comprise of necessity a substantial firebrick setting having a large heat capacity. When the plant is shut down and the fire withdrawn this brickwork is very hot and,

were the flow of oil to be then stopped, overheating would result, together with cracking of the oil and deposition of carbon. The shutting down must, therefore, be so arranged that, on withdrawal of the fire, there still remains sufficient oil to cool down the plant. It is here that a by-pass from the coolers to the benzolised oil tank is again a decided advantage, but the oil need not be diverted in this way until its temperature on leaving the still or column is  $100^{\circ}$  C. Live steam is then turned off and the oil diverted. In the absence of such a by-pass sufficient oil must be left for circulation until cool. When using a Wilton dehydrating coil for debenzolising, the author found that the temperature of the oil leaving the coil was still well over  $90^{\circ}$  C. one hour after drawing the fire, the oil being circulated at the usual rate in the meantime. Such tar dehydrators are usually provided with means for circulating water for cooling purposes, but this is obviously inadvisable when the plant is in use for debenzolising wash-oil.

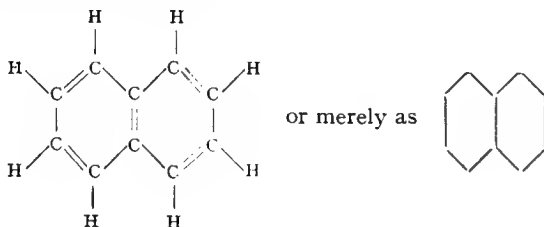
### Gas-heated Plant

A debenzolising plant heated by gas presents a case midway between coke-fired and steam-heated stills, in that greater regularity of operation is possible owing to the absence of clinking and firing. The same remarks as to overheating and shutting down apply here. When the combustion of the gas takes place in flue tubes immersed in the oil, as in the Hird-Chambers plant, care must be taken to obtain a Bunsen flame of medium length. A very short flame is apt to result in local overheating, whilst too long a flame is less efficient, and not only tends to give imperfect combustion, but also destroys to some extent the counter-current character of the heating process.

## CHAPTER VII

### DEPHLEGMATION AND THE NAPHTHALENE QUESTION

NAPHTHALENE,  $C_{10}H_8$ , is a double-ring hydrocarbon formed by the condensation of two benzene nuclei, its formula being usually written as follows :—



It is, at ordinary temperatures, a white crystalline solid, melting at  $79.6^{\circ}\text{C}$ . and boiling at  $218^{\circ}\text{C}$ . The specific gravity of the solid at  $15^{\circ}\text{C}$ . is 1.15, and that of the liquid at  $80^{\circ}\text{C}$ . is 0.977. Though insoluble in water, naphthalene will dissolve freely in most oils and other organic liquids. The solid hydrocarbon has a very high vapour pressure and may be readily sublimed. Conversely, the cooling of naphthalene vapour results in the deposition of exceedingly light crystals, remarkable for the relatively enormous space occupied per unit weight.

#### Naphthalene : Its Formation and Deposition

Naphthalene is essentially a high-temperature product. It is not found among the primary products of carbonisation, nor is it formed during the low-temperature distillation of coal. The compound is clearly, therefore, the result of cracking the vapours of other hydrocarbons, and, in fact, Cobb and Dufton, in the research previously mentioned, observed its formation on passing toluene through a tube heated to  $750^{\circ}\text{C}$ . and in an atmosphere of nitrogen. Continuous vertical retorts give approximately low-temperature products for the rich primary vapours are seldom subjected to great heat. It is not surprising, therefore, that the gas and tar from such retorts contain only traces of naphthalene, the maximum yield of which may be said to occur in a horizontal retort, lightly charged and maintained at a high temperature. A "packed" horizontal gives a naphthalene yield midway between

these cases, owing to the greater speed of travel of the gases from the retort, and to the lessened effects of radiation, as well as to the proportionately greater reduction of the retort temperature on introducing the charge.

In considering the formation of naphthalene, it is not out of place to mention the adverse effect in this respect of local overheating of the retorts, such as, for instance, is produced by "overpulling." Under such conditions producer and waste gases are pulled in through the pores and cracks in the retort, and cause very high temperatures locally, particularly when the gas so introduced contains oxygen. This is well known to produce a tendency towards naphthalene formation.

The question of the deposition of naphthalene in mains and services brings us again to considerations of vapour pressure. Although the vapour pressure of naphthalene is high compared with other solids, it is, of course, much lower than that of benzene and similar liquids; and, in consequence a very much smaller quantity of the former will suffice to saturate a given volume of gas at any particular temperature. J. S. G. Thomas (*Gas World*, December 28th, 1915, p. 701), who has corroborated the results of other workers, gives the following useful table.

TABLE 20.—NAPHTHALENE IN COAL GAS (*Thomas*).

Temperature. °C.	Vapour pressure of naphthalene. Mm. Mercury.	Grains of naphthalene to saturate 100 cubic feet dry coal-gas (measured at 15° C. and 760 mm.).
0	0.0056	1.75
5	0.0101	3.15
10	0.0176	5.49
15	0.0301	9.39
20	0.0506	15.8
25	0.0836	26.1
30	0.136	42.4
35	0.218	68
40	0.343	107
45	0.533	166
50	0.816	254
55	1.23	383
60	1.84	574

It is clear that before any solid naphthalene can be deposited the gas must be saturated with its vapour. Consider, for example, a coal-gas containing 9.4 grains of naphthalene per 100 cubic feet and at a temperature of 18° C. This quantity is too little to saturate the gas at that temperature, and therefore no naphthalene will be deposited on cooling to 15° C. Deposition begins



there, however, and between this temperature and  $10^{\circ}\text{C}$ . 3.9 grains of naphthalene will come down from every 100 cubic feet of the gas, which will then be saturated at  $10^{\circ}\text{C}$ .

This quantity of deposit appears somewhat small, but owing to its great bulk and to the facility with which it will adhere to a rough surface it is in fact serious, and a comparatively few grains of naphthalene will often cause acute trouble. Alwyne Meade points out that 10 grains of the hydrocarbon will completely block a  $\frac{1}{2}$ -inch pipe for a length of about 1 foot.

### Naphthalene and Oil Washing

Prior to the introduction of benzol recovery at gasworks, naphthalene trouble was never associated with the process; the reason being that, at coke-oven plants (to which the application of oil washing was restricted) little cause exists to draw attention to the subject. After the recovery of the by-products coke-oven gas is invariably utilised on or near the carbonising plant. A proportion—usually about 45 per cent.—is used for heating the ovens themselves, and the surplus is either burned under boilers or in gas engines, or otherwise disposed of, in the immediate vicinity of the plant. This means that the distributory system comprises relatively short lengths of large-diameter pipes, and the conditions are therefore conducive to freedom from stoppages. On the other hand, naphthalene has been a bugbear to gas engineers for many years. The distribution of "town" gas through long mains and finally through service pipes of small diameter offers to the naphthalene every facility to prove itself a nuisance, and the problem of effectively combating this trouble has proved very difficult of solution.

On the adoption of oil washing at gasworks, many of the undertakings concerned experienced an alarming increase in the number of naphthalene stoppages reported in the district, and this has undoubtedly created a general impression that benzol recovery entails this trouble. This, however, is by no means true. Many such cases were investigated by the author, and in only comparatively few could the stoppages be directly attributed to the addition of naphthalene to the gas by the wash-oil. It may here be remarked that some of the stoppages reported under this head were not due to naphthalene at all, but were caused by other constituents of the gas—particularly to excessive air unavoidably introduced, through wartime conditions and the bad state of repair of retorts and other plant. In one instance a stoppage was attributed to naphthalene, but an analysis of the deposit in the pipe gave the following result:—

	Per cent.
Naphthalene . . . . .	2.5
Cyanides (as $\text{K}_4\text{Fe}(\text{CN})_6$ ) . . . . .	0.7
Sulphur and tarry matter . . . . .	0.8
Iron oxide (and alumina) . . . . .	77.4

In a number of cases the naphthalene trouble was evidently directly due to oil washing, and the naphthalene content of the gas was actually increased through various causes, chiefly the use of warm oil or of oil containing an excessive percentage of the compound.

The majority of works where acute trouble was experienced, however, were found to be sending out the same, or a slightly lower, quantity of naphthalene, accompanied by a proportion of hydrocarbon vapours considerably reduced by the recovery process. In yet other cases the trouble was conclusively proved to be due to old deposits of naphthalene in the distributing system. Many of these deposits resulted from the previous operation of the "C" process, with its preferential absorption of "carriers" owing to the limited make of tar available for washing. In one large undertaking, no trace of naphthalene could be found in the gas leaving the works for nearly a year; yet towards the end of this period, 0.56 per cent. of the consumers per month were complaining of stopped services. The removal of this state of affairs is practically a question of time only.

### "Carriers"

If the quantity of naphthalene found from *Table 20* were deposited alone, the position would be indeed serious, but fortu-

TABLE 21.—NAPHTHALENE AND LIGHT OILS IN GAS AND TAR.

Works.	Naphthalene trouble.	Average naphthalene in gas. Grains/100 cubic feet.	Volume of light oils, 130°—170° C. Cubic centimetres per 100 cubic feet gas.			Cubic centimetres light oil, 130°—170° C., per grain of naphthalene in the gas.		
			In gas.	In tar.	Total.	In gas.	In tar.	Total.
A	None . . . . .	6.6	6.0	3.9	9.9	0.91	0.59	1.50
B	None . . . . .	13.7	5.0	4.1	9.1	0.37	0.30	0.67
C	None . . . . .	10.4	7.2	4.4	11.6	0.69	0.42	1.11
D	Serious. Mainly in district . . . . .	7.5	3.2	2.7	5.9	0.43	0.36	0.79
E	Serious. Works and district . . . . .	11.0	4.6	3.0	7.6	0.42	0.27	0.69
F	Serious. More on works than district	18.3	4.4	2.9	7.3	0.24	0.16	0.40

nately a quantity of naphthas, in which naphthalene is freely soluble, comes down simultaneously. These hydrocarbons are referred to frequently as naphthalene "carriers," and this expression is rather an unfortunate one. It appears to have given rise to an impression that the presence of such vapours in the gas assists the naphthalene, whilst as vapour, towards the consumer's burner. The fact is, however, that these liquid hydrocarbons do not become carriers, nor do they in any way affect the behaviour of the naphthalene until both they and it are condensed out of the gas. The extraction of these carriers (as crude benzol) in greater proportion than the naphthalene removed is, no doubt, the chief reason for the occurrence of the difficulty. Attention was called to their importance in Dr. H. G. Colman's most interesting report to the Southern District Association of Gas Engineers (*Gas World*, March 19, 1904, p. 499). Six works (among others) were investigated, in each of which the gas contained a comparatively high proportion of naphthalene; three of the works experienced much trouble, but the remaining three were immune. The figures in *Table 21*, based upon the report, will be quite sufficient to emphasise the connection between naphthalene and its "carriers."

### Prevention

Liability to naphthalene trouble will therefore usually depend upon the quantities of naphthalene and of hydrocarbon vapours contained in the gas, as well as upon external influences such as weather conditions, etc. As regards the gas, normal naphthalene contents are :—

Horizontal retorts	.	5—9	grains per 100 cubic feet.
Inclined retorts	.	4—5	" "
Vertical retorts	.	<i>Nil</i> —2	" "
Coke-ovens	.	5—6	" "

In connection with oil washing this figure is of importance, and it may be said that, in general, the process tends to increase a low naphthalene content and to reduce a high one. This means, of course, that the vapour pressure of naphthalene in average creosote is about equal, under average conditions of temperature, to its partial pressure in a normal coal-gas.

Avoidance of naphthalene trouble evidently necessitates an increase of the proportion of carriers to naphthalene, and this may be brought about by (a) reduction of the latter compound, or (b) addition of suitable hydrocarbons. Many processes for the extraction of naphthalene have been proposed and used; Ferguson Bell washes the gas with warm tar, finally treating it with a naphtha fraction; and Colson uses a light creosote in a Livesey washer. On coke-oven works abrupt and drastic condensation is resorted to, but this, together with many of the washing processes tends also to reduce the carriers present, as

well as the quality of the gas. To overcome this, other workers have washed with benzolised green-oil, but probably the most effective material for the purpose is carburetted water-gas tar. The latter liquid serves the double purpose of extracting naphthalene and adding hydrocarbons, but it is doubtful whether its use in a Livesey washer is very effective owing to low time-contact. It must also be remembered that the hydrocarbons added are usually benzols and paraffins of relatively low boiling point, and therefore less effective as carriers than the heavier ones.

Such a washing process should preferably be performed immediately before the holders, and must in any case come after the benzol scrubbers. Blue water-gas contains practically no naphthalene and its addition is therefore of use as a diluent; in other words, it enables the mixed gas to be cooled to a lower temperature before crystals will be deposited, but at the same time the amount of carriers is reduced in the same proportion. On the other hand, carburetted water-gas—which contains very little naphthalene unless the temperature of the superheater is excessive—not only acts as a diluent to the naphthalene, but also adds hydrocarbon vapours to the gas, and is in consequence, an undoubted advantage.

Whilst discussing the effect of carriers, the solubility of naphthalene in various liquids is of interest. These are approximately as follows:—

TABLE 22.—SOLUBILITY OF NAPHTHALENE.

SOLVENT.	Specific Gravity.	Approximate boiling range. °C.	Solubility of Naphthalene. Per cent.
Benzol . . . .	·880	80—100	54
Solvent naphtha . .	·875	120—160	35
White spirit . . . .	·760	80—90	25
Kerosene . . . .	·810	160—240	12—15

### Washing and Vaporising

For washing purposes heavy crude naphthas are often sold under trade names; and these are probably the most efficient materials to use, provided their original naphthalene contents are low. For addition to the gas, on the other hand, a liquid should be chosen having a boiling point and vapour pressure approximating to those of naphthalene, in order that the two may be deposited together. Benzol and other liquids of high vapour pressure are obviously of little use, since a very large quantity would be required to saturate the gas even at low temperatures; a smaller quantity would remain as vapour and consequently be of very little use. It would appear from theory

that ordinary paraffin oil or kerosene would be a very suitable material, and this is amply borne out in practice, very good results having been obtained with this oil.

The addition of hydrocarbons, such as kerosene, to the gas may be effected by evaporation or by atomising in the form of a fine spray. For evaporation several forms of apparatus are available, a typical and efficient one being Messrs. W. Parkinson & Co.'s vaporiser (FIG. 43). This is made in several sizes, and

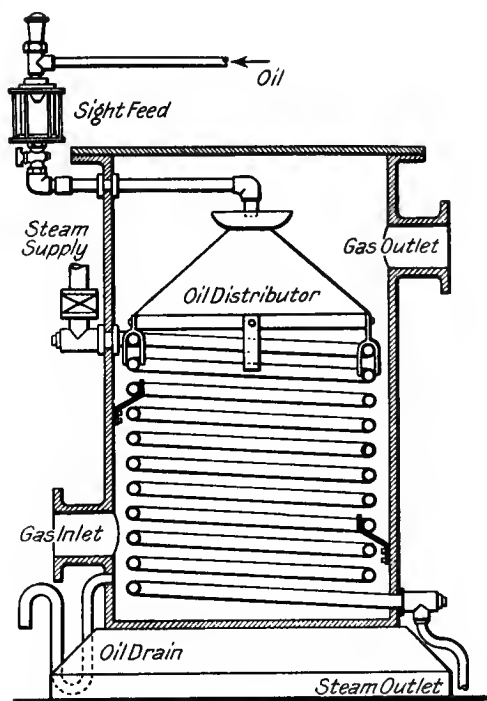


FIG. 43.—PARKINSON VAPORISER.

consists of a cast-iron cylinder containing a copper steam coil, which is supplied with steam at 60—80 lbs. per square inch, and over which kerosene drips from a distributing cone. The oil is supplied through a sight-feed, and a portion of the gas is passed through the cylinder. FIG. 44 shows another very good design, the "Simplex" vaporiser of Messrs. Robert Dempster & Son. This is also fitted on a by-pass, and by means of cast guides the oil is caused to take a long zig-zag course over a hot plate, which forms the upper side of a steam chest. The gas passes over the surface of the heated oil, and its flow is maintained by a steam

injector in the outlet pipe. Since moisture favours the deposition of naphthalene it would be better if this injector were replaced by some other device, or worked with compressed gas. Alternatively the gas may be forced through the by-pass and vaporiser by the differential pressure caused by a butterfly valve inserted in the main; where only one governor is in use the by-pass can most conveniently be taken from the inlet to the outlet of this, the governor then replacing the butterfly valve.

Many gasworks possess relics of the old benzol enriching days in the shape of maxim carburettors, and J. Bond has shown how these appliances may be easily converted into paraffin vaporisers. The apparatus is reversed, steam being admitted into the interior of the tubes and oil sprayed on their upper ends. Gas is passed around the tubes and the surplus oil runs back to the tank for recirculation. Such a contrivance, shown diagrammatically in FIG. 45, has given excellent results for a long period.

A vaporiser should preferably be installed at the outlet of the station-governors, unless blockages have been experienced in the holder connections, when it may be fixed between these and the station meters. Kerosene is probably the best and cheapest oil for the purpose, and the quantity to be used varies with the severity of the trouble from 5 to 20 gallons per million cubic feet of gas. When the hot carburetted gas mixes with the main stream it is chilled, and arrangements should be made for this to take place as quickly as possible. In this way much of the kerosene which condenses remains as a very fine mist instead of falling to the syphons. It may here be pointed out that the addition of paraffin also tends to preserve the meters in the district by preventing corrosion and by keeping the diaphragms of dry meters in good condition.

### Atomising

Paraffin may also be injected in the form of a spray or mist, either by pumping it at high pressure through a suitable spraying jet or by atomising it by means of a stream of compressed air or gas. The well-known systems of Botley and of Simmonds employ air, but in the writer's opinion this cannot be too strongly condemned. Every effort should be made to reduce the "inerts" in the gas, and the presence of oxygen tends towards corrosion of meters and services; compressed gas, which is equally effective, should, therefore, always be used. A very simple and efficient form of paraffin atomiser is shown in FIG. 46, through the courtesy of W. Doig Gibb, who was responsible for its design and application. The arrangement consists of a  $\frac{1}{4}$ -inch tube inside one of  $\frac{3}{4}$ -inch diameter. The outer tube has a 0.2-inch hole on the centre line of the main, and concentric with this is a hole of 0.1-inch diameter in the smaller tube, which is supplied with gas at 25 lbs. per square inch. From an overhead

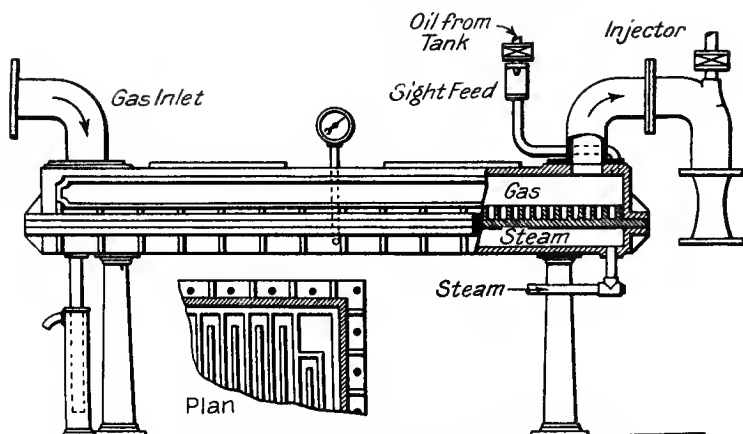


FIG. 44.—"SIMPLEX" VAPORISER.  
(Robert Dempster & Son.)

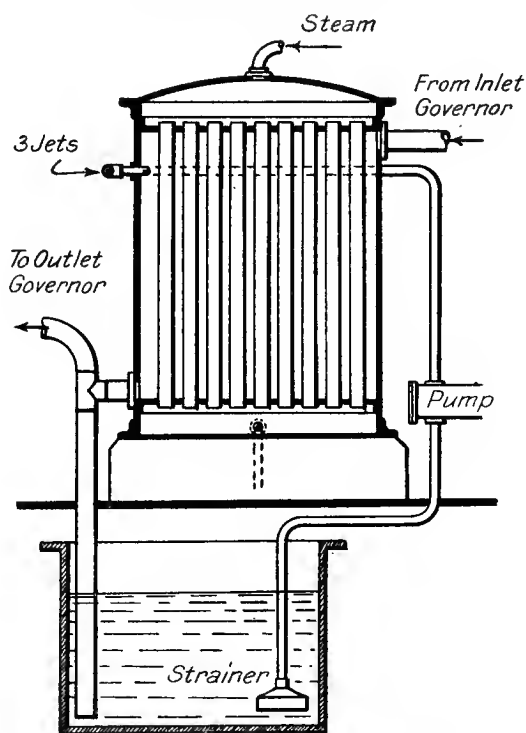


FIG. 45.—REVERSED MAXIM CARBURETTOR.

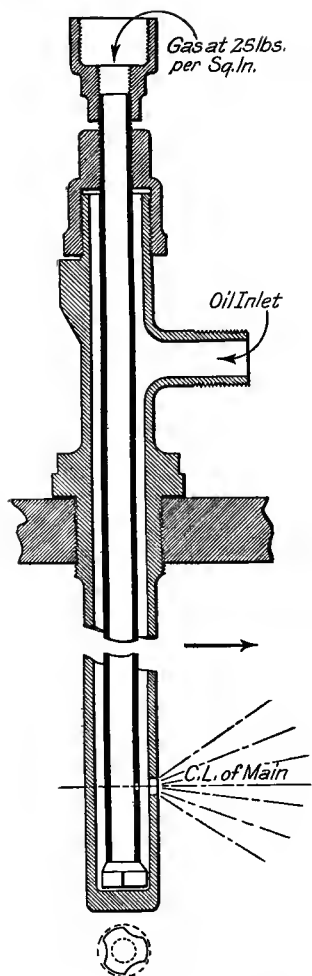


FIG. 46.—PARAFFIN ATOMISER.

tank, paraffin is admitted to the annular space between the tubes, and the result is an exceedingly fine mist of oil introduced at the centre of the main in the direction of the gas flow. This apparatus has been adopted at many works, large and small, and has given the utmost satisfaction.

A spraying apparatus should be fixed at the outlet of the governors, and the spray should be injected *in the direction of the gas flow*. Every effort should be made to select a position at the beginning of a long straight run of main, in order to avoid the precipitation of the mist after formation, through its impinging on sharp bends or other surfaces.

As regards the relative advantages of spraying and vaporising, there is little reason, apart from local conditions, to prefer either apparatus. An atomiser enables a quantity of paraffin to be injected in excess of that required to saturate the gas, and for this reason should possibly be preferred in cases of acute trouble. It must not be forgotten, however, that the gas passing through an efficient vaporiser is saturated at a relatively high temperature. If the cooling by admixture with the main stream of gas is sufficiently sudden the excess of oil remains in suspension as a fine mist. In both cases the mist formed must be exceedingly

fine, and in that condition will carry for miles. A coarser mist will tend to come down in the syphons immediately following the apparatus.

### Elimination of Naphthalene during Benzol Recovery

Whilst all the foregoing processes for reducing the liability to naphthalene trouble are more or less effective, their adoption



in each case entails expense and trouble, and no reason exists why the benzol scrubber should not be used also for naphthalene recovery. By ensuring a low naphthalene content of the entering wash-oil, with a correspondingly lower vapour pressure, a transfer of naphthalene from gas to oil may be effected. The writer has records of as much as 15 grains per 100 cubic feet extracted in this way along with the benzol. In spite of the abstraction of the "carriers" from the gas, the ratio of naphthalene to these may often be actually decreased, and in nearly every case prevented from increasing. To effect this it is, of course, necessary to use sufficient open steam during the debenzolising process to drive off the naphthalene. The consequences as regards naphthalene are admirable, but, otherwise, are a poor quality of crude benzol and rapid thickening of the wash-oil. To avoid these effects the

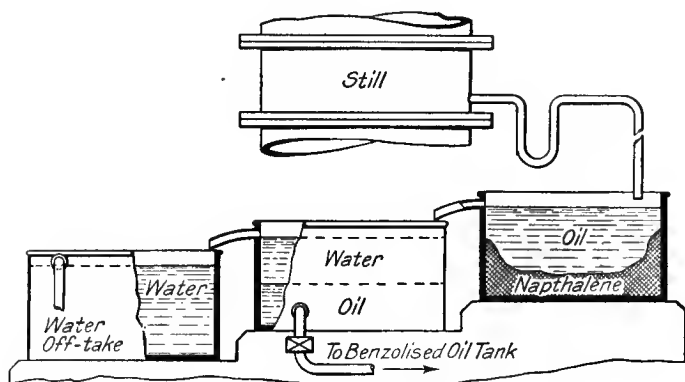


FIG. 47.—ARRANGEMENT OF TANKS FOR SEPARATING WATER AND NAPHTHALENE FROM CONDENSATE.

upper portion of the still may be left unlagged, and a condensate taken from the tray next, or next but one, above the hot oil inlet. This condensate consists of water and oil rich in naphthalene. After separation and settling out of the latter by cooling, the remaining oil is returned to the benzolised oil tank, and the naphthalene strained, pressed and sold. Suitable settling tanks for the separation of the water and naphthalene are shown in FIG. 47; such tanks should be of cast- or wrought-iron in preference to concrete to facilitate rapid cooling, and should be as shallow as possible. FIG. 35 (p. 82) shows the addition of a naphthalene off-take to a "Southport" column.

### Removal by Means of Dephlegmator

Whilst the removal of naphthalene in a condensate taken direct from the still is excellent, and a great advantage when

compared with the alternative procedure of making a weak benzol which shall contain the naphthalene of the wash-oil, a further refinement is reached by the adoption of a separate dephlegmator. This method is more scientific and furnishes a readier and more easily controlled application of theory. The vapours leaving the still are passed through a primary condenser, analyser or dephlegmator, which may be cooled by air, ingoing wash-oil or water. The last means is by far the best since it gives greater control over the qualities of benzol and condensate produced. Here the naphthalene is condensed together with a sufficient quantity of heavy solvent naphtha to keep it in solution, the liquid being run off whilst hot to a suitable system of separating and settling tanks as before described.

The application of this method to a steam-heated benzol plant is described by H. E. Copp in a paper read before the Midland

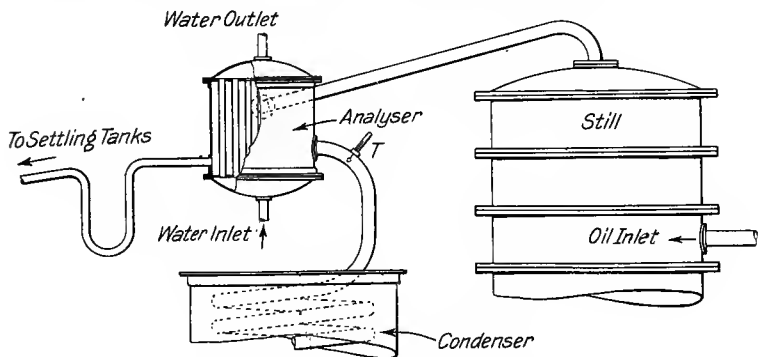


FIG. 48.—H. E. COPP'S APPARATUS FOR ELIMINATION OF NAPHTHALENE.

Association of Gas Managers (*Gas World*, November 2nd, 1918, p. 265; November 9th, p. 276), and his arrangement of the apparatus is shown in FIG. 48.

A small tubular and water-cooled analyser is interposed in the vapour pipe between the still and the condenser. The vapours pass around the water tubes in a downward direction, and are taken off to the condenser by a pipe which joins the body of the analyser a few inches above the bottom tube plate. The space between this vapour pipe and the tube plate serves to collect the condensate running down the water tubes, and the liquid is taken off, through a sealed U pipe, to the settling tanks. This arrangement, which the author has had the opportunity of examining, gives excellent results. The secret of success appears to lie in the careful regulation of the benzolised oil and open steam entering the still, and of the cooling water passing through the tubes. The oil and steam supplies are kept constant by a reducing valve on the main steam pipe serving pumps and live steam cock,

and the flow of cooling water is so regulated as to give a constant temperature of  $96^{\circ}\text{C}$ . on the thermometer T fixed in the vapours leaving the analyser. This temperature, found by experiment, may be understood by reference to *Table 14* (p. 28). Remembering that steam is present in the vapours it is obvious that the bulk of the naphthalene will condense on cooling to  $96^{\circ}\text{C}$ ., whilst the xylenes and lower-boiling hydrocarbons will pass on as vapour. The need for a constant proportion of open steam to benzol

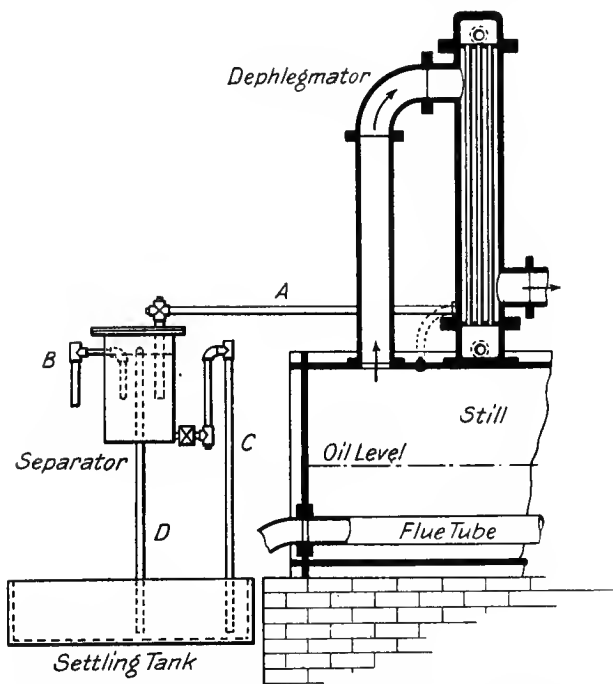


FIG. 49.—J. W. BREARLEY'S APPARATUS FOR ELIMINATION OF NAPHTHALENE.

vapours, attained by means of the reducing valve, etc., is also indicated by our consideration of the theory of steam distillation, and any excess or deficiency of steam will at once destroy the balance of the process by giving altered boiling points and a greater or smaller proportion of naphthas to naphthalene. The actual result of the adoption of this arrangement by H. E. Copp has been, for many months, a constant and higher quality of crude benzol, and a practically complete elimination of naphthalene from the wash-oil and, consequently, from the gas. In addition to this the wash-oil lasts much longer and is a more active

absorbent. The naphthalene content of the gas entering the oil washer averages 16.8 grains per 100 cubic feet, and this is reduced by oil-washing to *nil*—or at any rate, a quantity too small to be estimated. Of this naphthalene, 16 grains are recovered at the analyser and the remaining 0.8 grain goes forward into the benzol. Naphthalene troubles, formerly acute, have practically disappeared, and the injection of paraffin vapour has been discontinued. With such a high naphthalene content of the original gas, the simplicity and efficiency of the process are remarkably interesting. It is also of interest to note that very little but naphthalene and water appears in the settling tank; the crude naphthalene on cooling being accompanied by only a trace of oil.

This principle has been applied independently to a direct-fired benzol plant by J. W. Brearley (*Gas World*, March 31st, 1917, p. 254) in a very simple apparatus of which, also, the author has had experience. The plant in question is a Hird-Chambers dehydrating still, fired by coke-breeze, and adapted for debenzolising by the addition of open steam jets and a dephlegmator. The latter, which is tubular and water-cooled, was originally so arranged as to reflux naphthalene and heavy naphthas into the still. Such an arrangement made it impossible to eliminate naphthalene without producing a very poor benzol and, in consequence, rapidly thickening wash-oil. The apparatus was, therefore, altered as shown in FIG. 49. The condensate from the dephlegmator was diverted from the still, and led by pipe A into a small separator. It is here separated whilst hot, the water running away by pipe B, and the solution of naphthalene in oil to shallow settling tanks, *viâ* pipe C or D. The water, as will be noticed, is taken from the middle of the separating pot and the oil pipes leave the top and bottom of the separator respectively. The reason for this arrangement is found in the varying specific gravity of the hot condensate. When fairly new oil is in use this is occasionally lighter than water and must be removed by pipe D. Normally, however, and particularly when the wash-oil is becoming "spent," the oil forms the heavier portion of the condensate and is then run off through C. In this ingenious manner one separator is made to function under all conditions. The results attained by this apparatus have also been most satisfactory, and there is practically no loss of benzol from the separator and settling tanks, since the oil portion of the condensate, which is returned after cooling to the wash-oil, never gives more than 3 per cent. distillate at 120° C.—usually nearer 0.5 per cent. A more rapid crystallisation of the naphthalene is now obtained, by the recent addition of a small secondary still, worked intermittently and without live steam. In this the solution of naphthalene is concentrated before passing to the cooling tanks.

L. Trewby (*Gas World*, January 20th, 1917, p. 40) also uses a

small secondary still, but on a different principle. He prefers to make a low quality of crude benzol, containing practically all the naphthalene; the whole of the crude passes from the separator through a small continuous still, giving a high quality of benzol and a heavy residue which, after crystallisation of naphthalene, is returned to the wash-oil.

Since the introduction of the foregoing methods, some makers of debenzolising plant, notably the Chemical Engineering Co. and Messrs. R. and J. Dempster, have added secondary condensers to their designs.

### Old Deposits

Although naphthalene can be, and in many cases has been, entirely eliminated from the gas by the process described above, stoppages have nevertheless sometimes occurred; and in every such case the trouble has been traced to old deposits in the mains. To quote one instance, the gas leaving a fairly large works showed no trace of naphthalene for many months, yet at a point two miles away 5—6 grains per 100 cubic feet were regularly found. The cessation of this trouble is practically a question of time, but it is obvious that the injection of paraffin will be of material help. Where such old deposits are suspected, therefore, or where previous naphthalene trouble has been experienced, the commencement of oil washing should always be preceded by the installation of a paraffin spray or vaporiser. It is quite hopeless to wait until the appearance of stoppages before adopting remedial measures. The old saying that prevention is better than cure applies with particular force in this case, and Mr. Doig Gibb has pointed out that "patience is as necessary as brains" in solving this problem. Relief cannot be expected immediately, for when once the naphthalene has been deposited in the system its only means of exit are as a vapour through the consumer's burners, and dissolved in the oil pumped from the syphons. In this connection it is as well to emphasise the folly of clearing services by blowing the deposit back into the main, either by force pump or cartridge. Wherever possible services should be blown *from the main end*; if this be impracticable, and blowing from the consumer's meter unavoidable, the air should be preceded by a quantity of a suitable solvent.

Finally, a note of warning as to the use of a dephlegmator may be sounded. In many cases the installation of this portion of the debenzolising plant has been followed by the recovery of large quantities of naphthalene, which, however, have quickly fallen off. It has been concluded that the dephlegmator was not working properly, whereas the reverse was actually the case. The true explanation is that the oil has first been stripped of a high naphthalene content, the quantity finally recovered being the amount continuously extracted from the gas only.

## Naphthalene Tests

The estimation of naphthalene in oils has been described on p. 58. Its determination in gas is carried out by the method devised by Dr. H. G. Colman, and it must be particularly remembered that naphthalene is readily absorbed by rubber. For this reason the gas must not come into contact with any material amount of rubber tubing before entering the absorbing vessels. About 10 cubic feet of gas are passed at the rate of 1 cubic foot per hour, through four wash-bottles. The first is of glass throughout, and contains a 10 per cent. solution of citric

acid. The second bottle is charged with 100 c.c. of  $\frac{N}{20}$  picric

acid, the third with 50 c.c. of the same solution, whilst the last bottle serves as a "catch." The gas is then led to a test meter, and the supply of gas to the first wash bottle should be taken from a tee-piece, the remaining arm of which is connected to a burner in order to secure a brisk flow of gas through the various connections. After passage of the requisite volume of gas—which is corrected for temperature and pressure in the usual way—the contents of the second picric acid bottle, and any solution carried over into the catch, are washed into the first picric acid bottle, which is then closed and evacuated by means of a pump. This bottle is heated in a water bath until all the naphthalene picrate has dissolved, and allowed to cool completely with occasional shaking. When cold, the contents of the bottle are poured into a 250-c.c. measuring cylinder and the total volume noted. The precipitate is separated by filtration, the first few cubic centimetres of the filtrate being rejected. The remainder is collected and 100 c.c. of it titrated with decinormal soda, using lacmoid or phenolphthalein as an indicator. The original picric acid was

equivalent to 75 c.c. of  $\frac{N}{10}$  soda. From the titration the volume

of  $\frac{N}{10}$  soda required to neutralise the picric acid in the whole of the filtrate may be found. If  $V$  = the difference between this figure and 75, then :

Grains of naphthalene per 100 cubic feet =

$$\frac{V \times 100 \times 0.1975}{\text{Corrected volume of gas passed}}$$

## CHAPTER VIII

### PRECAUTIONS AND DIFFICULTIES IN WORKING

#### Fire

AT the outset it is obvious that the most thorough precautions must be taken against fire. Owing to the highly inflammable nature of benzol and of the other materials handled, the necessity for the greatest care is apparent, and little need be said on the subject except to point out the desirability of keeping all benzol, separators, etc., as far away from the grate of a direct-fired plant as possible.

#### Naphthalene

Naphthalene may give rise to certain difficulties, and these, together with the precautions to be taken in this connection, have been dealt with in the preceding chapter. Though it is advisable, for reasons to be explained later, to keep the temperature of the oil entering the scrubber slightly higher than that of the gas, yet the former should not be too high. A warm oil tends to the addition of naphthalene to the gas.

#### Water in Oil

Water in oil, as distinct from emulsification, sometimes gives trouble and may usually be traced to a low temperature of the oil entering the still, or to the use in it of wet steam. In such cases the water usually separates out with ease on standing; but, whether in this form or in the form of an emulsion, water in oil is highly detrimental both to the scrubbing process and to the operation of debenzolising. The presence of water always reduces considerably the attainable temperature; and as a low oil temperature also favours the condensation of water, the effect is a cumulative one. The debenzolised oil leaving the coolers should not contain more than 0.5 per cent. of water, and this may usually be assured by maintaining the temperature of the oil leaving the still above  $100^{\circ}\text{C}$ . Preheaters must be efficient; intimate contact and counter-current flow are essential. The author recollects a "loop" preheater in which the oil could not be raised above  $117^{\circ}\text{C}$ . Baffle-plates were inserted with a view to carrying the oil into more intimate contact with the steam loops, when a temperature of  $137^{\circ}\text{C}$ . was easily attained with the

same rates of flow of oil and steam. Wet steam is a frequent cause of water in oil, the sensible heat of the latter being insufficient thoroughly to dry the steam. Lagging of steam pipes has been referred to repeatedly, but its importance fully warrants the repetition.

Provided no emulsification has occurred, the water may be easily separated from the oil, and the separation may be assisted

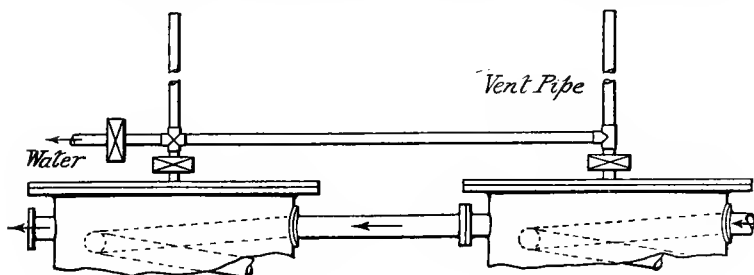


FIG. 50.—WATER OFF-TAKE ON HEAT EXCHANGER OF THE COIL TYPE.

by warming. To this end some designers add a water separator in the debenzolised oil connections between still and heat exchanger, whilst alternatively pipes may be fitted to take away water from the tops of heat exchangers in which it commonly separates. Such an arrangement is shown in FIG. 50. Neither of these devices should, however, be needed, and if this trouble is otherwise unavoidable, a closed steam coil in the base of the still will usually cure it.

### Emulsification

Emulsification is also due to the presence of water in the oil, but is somewhat different in origin as well as more difficult of removal. It is usually caused by the condensation of water (from the gas) in the scrubbers, where the more extended distribution of the water vapour and oil favours the condensation of the former into minute globules, which become coated with oil before they can coalesce. The remedy is, of course, to keep the temperature of the wash-oil higher than that of the gas. On account of the possibility of naphthalene trouble the difference should not exceed  $2^{\circ}$  or  $3^{\circ}$  C. An oil warmer is sometimes useful in this connection, particularly in cold weather or in cases where the gas temperature is unavoidably high. It may take the form of the well-known "Liebig's condenser," jacketed by exhaust steam from the pump instead of by water, and fitted with a large by-pass to regulate the temperature. Water is, however, often carried in suspension in the gas and this frequently comes down in the wash-oil, sometimes (but not usually) as an emulsion. In



this case every effort must be made to trap the moisture, and the first bay of a rotary scrubber may often be found more useful for this purpose than as the last oil bay of the benzol extractor.

Water present as an emulsion will not settle out at ordinary

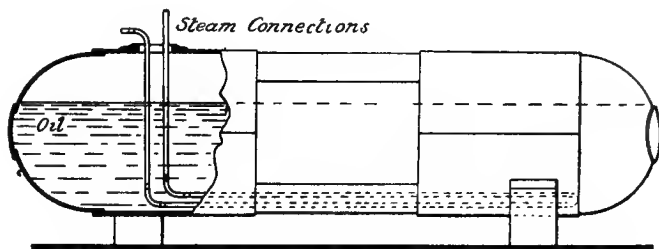
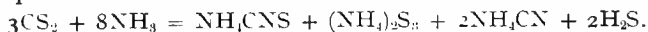


FIG. 51.—BREAKING UP A WATER-OIL EMULSION BY HEAT.

temperatures, even on prolonged standing. The only method of dealing with an emulsified oil appears to be to pump it into a separate tank, and there to heat it to a temperature of 40° or 50° C. for some days by means of a closed steam coil or loop. A suitable method of doing this is indicated in FIG. 51.

### Corrosion

Although wrought iron and mild steel may be safely used in the construction of benzol plants when purified gas only is scrubbed, yet if there is any trace of ammonia, hydrogen sulphide, etc., cast iron should be used throughout. This material is much less liable to attack, but even with it serious corrosion has sometimes occurred. The author has investigated many cases; it was noticed that corrosion only appeared when the gas—and, therefore, the wash-oil—contained ammonia, but since many refrigerating plants employ liquid ammonia and are constructed of steel, it was thought that this compound could scarcely be the cause of the trouble. Similarly, hydrogen sulphide can hardly be blamed, for little corrosion is experienced in a sulphate of ammonia still where both these gases exist in much greater concentration. The analysis of deposits from corroded preheaters always contained a fairly large proportion of cyanogen compounds, and these are, in fact, well known to be highly corrosive. From extended observations it would appear that the normal amount of cyanogen in coal-gas is practically harmless, and it may be that the cyanide compounds causing the trouble are actually the result of the well-known reaction between ammonia and carbon disulphide :



Unfortunately it has not yet been possible to verify this by

experiment. In any case it is fairly certain that corrosion is much reduced, if not entirely avoided, by eliminating all traces of ammonia from the gas before its entry into the oil scrubbers.

Sulphur, however, is also responsible for some of the corrosion, and the deposits previously referred to usually contained sulphides. It appears that this may be due to the action of complex organic sulphur compounds; and corrosion has often been associated with the use of paraffinoid wash-oils which, as explained in Chapter III., are particularly liable to the formation of such compounds.

The corrosion of tar-stills is commonly attributed to ammonium chloride, and under certain conditions this may also contribute to the destruction of benzol plants, whilst it is not inconceivable that sulphur dioxide might under certain other conditions, be present. Electrolysis, due to the proximity of dissimilar metals, has also been suggested as a reason. The whole subject is one which would repay careful investigation; in the present state of our knowledge it is certainly advisable to exclude all ammonia, and to keep the percentage of water in the wash-oil as low as possible.

### Leakage

Leakage may occur in various ways and positions on the plant. Its prevention is purely a mechanical question and the greatest care should be taken in making all joints. Leakage (*e.g.*, of steam into a preheater) is sometimes also brought about by corrosion, and such an occurrence is, as a rule, easily detected. Creosote and benzol penetrate the slightest "weep" very rapidly, and also cause trouble at times in valves, cocks, glands, etc., which should therefore receive regular attention.

### Solid Deposits

Solid deposits are due, in general, to one or more of three causes:—

- (a) Corrosion.
- (b) Separation of solid matter from the wash-oil.
- (c) Cracking of the oil (on direct-fired plants only).

Such deposits are difficult to avoid, and are best dealt with by the provision of suitable hand-holes and cleaning doors throughout the plant. It must be remembered that this solid matter, when deposited on steam-loops and coils, etc., acts as a heat insulator, and such parts of the apparatus should be cleared regularly. By-pass connections facilitate this operation in large plants; and where much trouble is experienced it is sometimes advisable to instal duplicate preheaters. Such parts of the apparatus as distributing jets in scrubbers should also be examined periodically, and for a somewhat similar reason the external surfaces of condenser coils and coolers should be occasionally

scraped and brushed. The frequency of this will vary with the type of apparatus and with the character of the water employed.

Naphthalene and anthracene deposits only occur in the coolers. The former may be cleared by steaming, but an anthracene stoppage frequently necessitates dismantling. A by-pass connection and run-off cock should always be provided on the oil coolers.

### Thickening of Wash-oil

Thickening of wash-oil, as has been stated previously, is one result of the steam distillation process, and is due to the extraction by this means of the lighter and more fluid constituents of the oil. The residue becomes more and more viscous, and consequently less efficient as a benzol absorbent, whilst the debenzolising process is also adversely affected. The effects of high viscosity may be delayed by the addition of new oil to the bulk at regular intervals, and it has been suggested that 10 per cent. of the oil be removed each week and replaced with new. This appears rather excessive when it is remembered that such renewals only delay, and do not obviate, the final rejection and replacement of the whole bulk. Moreover, it would appear advisable to add a specially light creosote (*i.e.*, one approximating in composition to the constituents lost) instead of a quantity of oil similar to that originally taken.

The total consumption of wash-oil on a number of plants of all sizes averaged, for steam plants, 25 per cent. of the crude benzol made, and 30 per cent. for direct-fired plant. These figures appear to represent fairly average conditions, but the cases considered included several in which water troubles were experienced. The averages are, therefore, probably on the high side.

### Air- and Vapour-locks

Air- and vapour-locks must be guarded against at every position in the plant. The effective manner in which a pocket of entrapped air or vapour will obstruct the flow of oil—even with such a back-pressure as has been known to “blow” a joint—has been referred to, together with the means of avoiding such trouble, when vent pipes were under consideration. The flow of oil should tend upwards wherever possible, and the outlet from any portion of the apparatus should be at its highest point. Where the oil flow is perforce taken in a downward direction a vent pipe must be fitted at the highest point of its travel; and when the oil passing the vent pipe is benzolised, the pipe should be connected up to the vapour pipe entering the condenser.

### Priming

Priming in the still is usually due either to water in the oil or to the use of a still too small for the quantity of wash-oil passed

through it. The elimination of water has been considered, and the effects of priming may be avoided by baffling the vapours in the top of the still. Suitable baffle-plates are shown in a column still in FIG. 33 (p. 78), and alternatively small catch pots may be added. The top compartment of a tray still may be allowed to remain empty as a baffle chamber.

### Oil in Purifiers

Where it has been necessary to scrub the gas for benzol prior to its entering the oxide purifiers, trouble has sometimes occurred through the carrying forward of particles of oil which, being deposited on the oxide, reduce its efficiency. Oil-fog may be

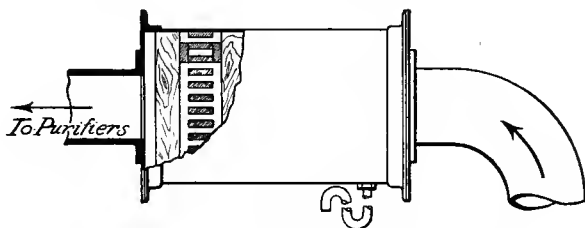


FIG. 52.—TRAP FOR FREEING GAS FROM OIL-FOG.

precipitated by a baffle chamber, fitted in the main immediately before the purifiers, and filled with boards similar to those in a tower scrubber or with coarse iron borings. A suitable arrangement, which has proved satisfactory in many instances, is shown in FIG. 52.

### Drying of Meter Diaphragms

During the war there was an alarming decrease in the useful life of the leather diaphragms used in consumers' dry meters, and this, in common with many similar ills, was by some people attributed to oil washing; the theory being, presumably, that the stripped gas had a greater drying action on the leathers, absorbing the oils with which they are treated and rendering them liable to attack by other constituents of the gas. Even if the presence of benzol could have any effect in keeping the diaphragms in an oily condition it is difficult to believe that the removal of such a comparatively small quantity of its vapour could make any serious difference. Moreover, the same trouble was experienced by gas undertakings who were not recovering benzol. It appeared, therefore, that the difficulty was due to some other wartime condition, and recent work, particularly that of Messrs. Parkinson and Taplay (*Gas World*, October 19th, 1918, pp. 213, 228—31), indicates that the general shortage of gas-oil might have been responsible.

## CHAPTER IX

### COST OF CRUDE BENZOL RECOVERY

THE present uncertainty as to the ultimate market price of benzol, and particularly as to the costs of both labour and material, renders a study of costs particularly difficult. For obvious reasons it is impossible to give reliable figures for the cost of benzol recovery on gasworks before the war. The author, therefore, proposes to give some general data on these points which will enable estimated balance sheets to be constructed, with due regard to the conditions existing at the time. A permanent rise in the market value of benzol products may be confidently anticipated, and it is quite certain that, even under present circumstances, the recovery of benzol may be regarded as a "paying proposition" on all but the very smallest gasworks. The items to be included on the debit side may be classified under the following heads, the various costs being given on a pre-war basis unless otherwise stated.

#### Cost of Plant

The capital outlay involved varies considerably with the degree of stripping desired, as well as with the system of debenzolising to be adopted. For the average gasworks, it may be taken that the cost of a plant for full recovery of benzol will be from £9 to £12 per ton of coal carbonised per (maximum) day, exclusive of scrubbers and boilers. The variation between summer and winter loads renders it necessary to instal a plant to deal with the maximum make of gas, and this is relatively costly; but this fact is an advantage in one respect, in that it enables a larger quantity of oil to be circulated per ton of coal in the summer, when higher atmospheric temperatures tend to reduce the efficiency of the scrubbers. A steam-heated plant will in general cost more than a direct-fired still of equal capacity, though the former is by far the more economical in working. As may be expected, the cost of the plant on the basis of a ton of coal or of benzol varies inversely with its size, and whilst a very large works might be equipped for benzol recovery for £8 per ton of coal per day, the same degree of stripping by a very small undertaking might entail an outlay of £12 or even £15 per ton of coal.

The pre-war cost of scrubbers may be taken as varying with the degree of stripping required from £4 to £8 per ton of coal per maximum day.

An annual charge of 17 per cent. on the total capital outlay will in most cases cover interest, depreciation and maintenance.

### Labour

Labour charges also vary considerably with the conditions obtaining in individual cases. It has been pointed out that by suitably arranging the plant and making it as automatic as possible very little labour is needed. Under these conditions a steam-heated benzol plant on a works carbonising up to 150 tons of coal per day should require no regular attendant. The only attention necessary, provided constant-head feeds, steam-reducing valves, etc., are applied, is a glance at the thermometers, steam gauges and pumps every one or two hours. In the great majority of gasworks it can be arranged that a man employed on other work—*e.g.*, a shift foreman or exhauster attendant—can carry out this periodical visit in addition to his other duties. In larger works a benzol plant attendant is desirable, but never more than one should be necessary, exclusive of boilermen. The writer has, in fact, had experience of a plant dealing with the gas from 700 tons of coal per twenty-four hours where the whole of the work was effectively performed by one woman per shift. It is therefore clear that a well-designed steam-heated plant may be run at very little cost so far as labour is concerned.

A direct-fired plant, on the other hand, requires constant attention, since the heating is far less uniform, and the fire requires feeding and clinkering. By erecting the still near another part of the plant, such as a sulphate of ammonia plant or boiler house, it is often possible to economise labour. Thus in one case a single man per shift suffices to work sulphate of ammonia, tar dehydration and crude benzol plants.

### Steam and Fuel

The cost of heating the oil is obviously a big proportion of the total cost of the process, since for every gallon of benzol produced some 25 to 30 gallons of wash-oil must be heated to about 120° C. and subsequently cooled. Every effort should, therefore, be made to secure as much economy as possible by means of heat exchangers. In a steam-heated plant with moderately good heat exchange the production of 1 ton of crude benzol necessitates the use of from 1½ to 2 tons of steam, or a steam cost of about £1 per ton of crude benzol. This assumes continuous working; starting up and shutting down of the plant are obviously wasteful from a thermal point of view.

A direct-fired plant usually costs rather less than this for fuel, though any saving in this respect is more than counterbalanced by the extra labour required. Using breeze in the furnace the fuel costs (excluding steam to the blowers) may be as low as

12s. or 15s. per ton of benzol. On the other hand, a still fired with coke and working during the daytime only has cost as much as £2 5s. per ton of benzol under this head.

In gas-fired plants, taking gas at a pre-war cost-price of 1s. per 1,000 cubic feet, the cost of heating is approximately the same as, or a little higher than, the charges for steam on a steam-heated unit.

### Water

The quantity of cooling water required varies considerably with the efficiency of the heat exchangers and of the coolers themselves. A totally immersed cooler requires from 30 to 40 gallons of water per gallon of crude benzol made, whilst for a cooler of the spray type the figure is reduced to from 20 to 30 gallons.

On the same basis the amount of condensing water necessary (assuming a distillate consisting half of benzol and half of water) is from  $1\frac{3}{4}$  to 2 gallons where there is no vapour/oil heat exchanger, and about  $1\frac{1}{2}$  gallons where this is installed.

### Wash-oil

The cost of wash-oil is also a comparatively heavy item in the total cost. As we have seen, the consumption of wash-oil rarely exceeds 25 per cent. of the crude benzol produced. With efficient dephlegmation, and particularly in those cases where the plant has been arranged for naphthalene extraction, as described in Chapter VII., this figure is substantially reduced, and may be as low as 15 per cent.

### Total Cost

Working on the above data it will usually be found that the actual cost of producing one gallon of crude benzol is from  $3\frac{1}{2}d.$  to  $5d.$  Most published balance sheets have added to this the cost of enriching the gas to its original quality, and as regards calorific value a gallon of gas-oil (as carburetted water-gas) is roughly equivalent to a gallon of benzol. In view, however, of the reports of the Gas Investigation Committee of the Institution of Gas Engineers and of the Fuel Research Board, such enrichment is obviously unnecessary. On the other hand, it appears likely that gas will in future be sold on a basis of thermal units, and in that case the process must be debited with the value of the benzol as gas. The supply of 500 B.Th.U. gas at  $4s. od.$  per 1,000 cubic feet is equivalent to selling 100,000 B.Th.U. for  $9\frac{1}{2}d.$  On this basis a gallon of crude benzol would represent about  $11d.$  since 75–80 per cent. of it is extracted from the gas. Obviously it will then be necessary to add this figure to the cost of the benzol. Even then, with the cost of rectification at about  $4d.$  per gallon, and a deduction for distribution expenses, it is obvious that benzol recovery will yield a handsome return.

# PART II

## THE RECTIFICATION OF BENZOL

### CHAPTER X

#### CRUDE BENZOL AND ITS USUAL PRODUCTS

OWING to the chemical similarity of the constituents of crude benzol, its analysis is a somewhat difficult problem. Many methods, mostly empirical, have been devised, and some of the best known are given below. The standard method, however, for the analysis of benzols and for the estimation of benzene, toluene and xylene in any tar or gas products is that devised, after a great deal of experimental work, by Dr. H. G. Colman. Owing to the importance of this method, and also for greater convenience, an abstract of the method as applied to the analysis of crude benzol is given in APPENDIX A. (p. 195). This has been taken from a paper read by Dr. Colman and E. W. Yeoman before the Society of Chemical Industry (*J. Soc. Chem. Ind.*, xxxviii., 6. 57, T.). Accurate results can, however, only be obtained by close adherence to the conditions of distillation, etc., laid down, for which sufficient space is not available here, and these must be obtained from the original paper.

A shorter method useful for approximate analysis is that of W. G. Adam. One litre of the benzol is carefully measured and distilled at a rate of 3 c.c. per minute through an ordinary fractionating column to  $180^{\circ}\text{C.}$ , the residue being creosote. The distillate is measured and washed with 120 c.c. of a saturated solution of sodium hydrate in alcohol and then with water, in order to remove carbon bisulphide, the amount of which is indicated by the reduction in volume. The liquid is then washed successively with concentrated sulphuric acid, caustic soda and water, and dried over calcium chloride. The dried oil is finally distilled at the same rate through a Young-Thomas still-head of eight sections, the following fractions being collected:—

- (a) Below  $85^{\circ}\text{C.}$
- (b)  $85^{\circ}$ — $105^{\circ}\text{C.}$
- (c)  $105^{\circ}$ — $115^{\circ}\text{C.}$
- (d)  $115^{\circ}$ — $165^{\circ}\text{C.}$



Provided carbon bisulphide and water have been entirely removed the volume of benzene present is represented by the quantity  $(a) + \frac{1}{2}(b)$ . Similarly, the toluol is given by  $\frac{1}{2}(b) + (c)$ , and the solvent naphtha by  $(d)$ . Paraffins are corrected for by the specific gravity method (*see* p. 131), and the proportion of creosote is found from the volume of the oil remaining at 165° C. plus the original residue.

A. Edwards uses a similar method, but adopts as cut-points those temperatures at which, according to theory, the hydrocarbons should distil in 50 per cent. mixtures. His fractions are accordingly:—

Up to 80.2° C.	.	.	Forerunnings.
80.2°—97.6° C.	.	.	Benzol.
97.6°—126.7° C.	.	.	Toluol.
126.7°—160° C.	.	.	Solvent naphtha.
Residue.	.	.	Creosote.

### Correction of Thermometers

In all distillation tests it is of the utmost importance that the thermometer used should be correctly calibrated. In other words, a correction must always be found which will include the original error in the thermometer itself, as well as corrections for barometric pressure and length of stem immersion for each particular test. For accurate work, *e.g.*, the analysis of benzol by Colman's method, this must be carried out carefully. The correction due to inaccuracy of the thermometer at different temperatures should be found by careful comparison of its readings with those of a standard thermometer in vapours of benzene, toluene, xylene, etc. The additional correction for conditions obtaining at the time of the test is found from well-known formulæ, which are given in APPENDIX B. (p. 200).

For works control tests and on other occasions when absolute accuracy is not essential, a composite correction may readily be found before each test, by boiling distilled water in the distillation flask, and exposing the thermometer to its vapour under the same conditions as will obtain in the test itself. The difference between the observed boiling point and 100° C. will then give directly the correction to be applied.

### Composition of Crude Benzol

The usual class of crude benzol produced by the oil-washing process is known as 65's crude, by which is meant that it will yield 65 per cent. of distillate below 120° C. by the retort test. In Chapter VI. (p. 97) this test has been described as unscientific and misleading. The test devised by the Department of Explosives Supply as a substitute for the retort method is a very big improvement, and is there fully described. A "normal"

crude benzol is one which gives 80 per cent. at 120° C. when tested by this method in a side-tube flask. Such a spirit corresponds roughly with the usual 65's benzol, and represents an average quality. The whole of the benzol produced by over a hundred gasworks during a period of six months was tested by this method, the average result being about 81 per cent.

The particular quality of benzol which it is found most advantageous to produce on a given plant varies, however, with local conditions, for it must be remembered that a high quality of product often results from badly stripped oil, which in turn means reduced absorption in the gas scrubbers. A low quality of benzol cannot in general be obtained unless the debenzolising of the oil is fairly complete; but, on the other hand, such low quality means a shorter life of the wash-oil, and also more material to transport to the rectifying plant for a given quantity of pure products. We may safely conclude, therefore, that when the rectification is carried out at or near the same works it will pay best to produce a quality of benzol lower than the average; for in such a case transport is negligible, and the heavy constituents of the crude may be cheaply returned to the wash-oil. If, however, the rectification is carried on at a distance "normal" crude benzol is usually the most profitable product. The presence or absence of a dephlegmator for naphthalene removal will, of course, have an important bearing on this question.

The composition of the crude spirit varies with certain factors, the chief of which are the class of coal carbonised, the system of carbonisation, and the design and working of the scrubbing and debenzolising plant. The average constitution of samples of crude benzol, from gasworks in all parts of the country using all classes of coal, is shown in *Table 23*.

TABLE 23.—COMPOSITION OF CRUDE BENZOL.

RETORTS EMPLOYED.	HORIZONTAL.		INCLINED.	VERTICAL.
	Steam.	Direct-fire.	Steam.	Steam.
Debenzolising plant.				
Specific gravity at 15.5° C.	0.896	0.899	0.875	0.873
Carbon bisulphide . . . .	0.5	0.3	0.3	0.3
Paraffins . . . . .	1.3	1.1	5.3	10.4
Benzene . . . . .	50.3	39.9	32.2	22.0
Toluene . . . . .	16.4	18.4	17.8	9.5
Xylenes . . . . .	8.0	10.2	13.6	16.7
Loss on alkali washing . . .	0.5	0.7	1.0	0.9
Loss on acid washing . . .	5.3	5.5	11.4	8.2
Residue at 170° C. in washed distillate . . . . .	2.9	3.7	6.9	6.9
Residue at 170° C. in original sample . . . . .	14.8	20.2	11.5	25.1

### Paraffins

These figures show very clearly the increase in paraffin content of the crude benzol, when the system of carbonisation changes successively from horizontal to inclined and vertical retorts, and it will be noted that this increase is accompanied by a decrease in the benzene contents, and an increase in the percentage of solvent naphtha and unsaturated hydrocarbons (the last being indicated by the "loss on acid washing" figure). Paraffins are a low-temperature primary product, and are more in evidence in vertical retort practice owing to the reduced amount of "cracking" to which the gas is subjected. The process of steaming vertical retorts has recently become very popular in consequence of its many advantages, which are themselves mainly attributable to less cracking and a more rapid removal of the gases from the retort. One would therefore expect to find a further increase of paraffins, at the expense of the benzene fraction, when steaming is adopted. This is actually the case in practice as reference to *Table 24* will show. These figures give the average composition of crude benzol from two

TABLE 24.—CRUDE BENZOL FROM "STEAMED" VERTICAL RETORTS.

GAS WORKS.	A.	B.
Specific gravity . .	0.853	0.856
Paraffins . . . .	15.9	12.6
Benzene . . . . .	15.0	30.8
Toluene . . . . .	11.2	11.6
Xylenes . . . . .	25.8	15.1
Loss on acid washing .	10.6	8.9

gasworks where steaming was being carried out in continuous vertical retorts.

The percentage of paraffins is only of commercial importance in the case of the pure products, and is therefore usually estimated from the specific gravity of those products, or the corresponding fractions obtained during analysis, *after the removal of carbon bisulphide*. In the case of the washed benzene fraction, allow 1 per cent. of paraffins for each 0.001 that the specific gravity of the liquid is below 0.873. For toluene, the corresponding figures are two-thirds of 1 per cent. for each 0.001 below 0.870, the specific gravities being of course taken at 15.5° C.

If it is desired to estimate the paraffin content of a sample of benzol directly, the spirit may be subjected to a prolonged boiling with concentrated sulphuric acid, under a reflux condenser. The benzols are sulphonated, and the residue may be taken as approximately representing the paraffins.

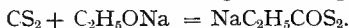
It is practically impossible to make paraffin-free pures from a crude spirit containing a high percentage of paraffins. For motor fuel, the presence of paraffins in rectified benzol is of no moment, but when the pure products are required for the manufacture of intermediates for the dye works, or of explosives, the paraffins must not be more than about 3 per cent. A higher percentage will cause trouble in the subsequent processes.

### Other Impurities

#### *Carbon Bisulphide.*

Carbon bisulphide is always present to a small extent in benzol obtained from gas washing. A very delicate qualitative test for this compound is the addition of a few drops of phenyl hydrazine to 10 c.c. of the sample. After shaking and standing for an hour the presence of  $\text{CS}_2$  is indicated by the formation of crystals.

For purposes of analysis this compound is removed from benzol by washing with sodium ethylate, or with a solution of caustic soda in industrial methylated spirit (free from paraffins). Sodium xanthate is formed according to the equation :



The xanthate is removed by shaking with successive quantities of water, and the spirit is dried with calcium chloride. The proportion of  $\text{CS}_2$  removed may be calculated from the specific gravities of the benzol before and after this operation, assuming that the specific gravity of pure  $\text{CS}_2$  is 1.27, and that no expansion or contraction occurs on its admixture with benzol.

#### *Thiophene*

Thiophene is detected qualitatively by the addition of a few drops of the sample to a little concentrated sulphuric acid containing a crystal of isatin. The presence of thiophene produces a blue colouration.

Thiophene,  $\text{C}_4\text{H}_4\text{S}$ , occurs in crude benzol to the extent of from 0.5 to 1.0 per cent., and usually forms about one-half of its total sulphur content. It is very similar to benzene in colour, odour and boiling point but, unlike the latter compound, is soluble in cold concentrated sulphuric acid. Whereas the bulk of the  $\text{CS}_2$  is removed by distillation (in the forerunnings), thiophene must be removed when necessary by an extra acid wash. This is only needed when the amount present is excessive, or when making pure products to a specification limiting the sulphur content (*e.g.*, motor benzol).

The determination of thiophene in benzol is made by the use of Denigés' reagent, which is prepared by adding 20 c.c. of concentrated sulphuric acid to 100 c.c. of water, and dissolving

5 grammes of mercuric oxide in the mixture. Two c.c. of the benzol under examination is shaken for six hours with 20 c.c. of this reagent. The white precipitate is then filtered through a tared Gooch crucible, washed with hot water until neutral, dried at  $110^{\circ}$ — $115^{\circ}$  C., and weighed. The weight of thiophene contained in the 2 c.c. of benzol is given by the weight of the precipitate multiplied by 0.0758.

### *Unsaturated Bodies*

Apart from an occasional trace of cyanogen compounds, and, where oil washing takes place before the oxide purifiers, a very small percentage of sulphuretted hydrogen, the only other impurities of importance are the unsaturated compounds—olefines, dienes, etc.—which are removed during acid washing, together with a little pyridine. Rectified products should be tested in order to ascertain whether acid washing has been complete. A quantity of the spirit is well shaken with one-tenth its volume of pure sulphuric acid for five minutes. The colouration of the acid layer after settling out should not be darker than that of decinormal potassium bichromate.

### **Usual Products Made**

Before the war a great variety of grades of rectified benzol, toluol and solvent naphtha was available, and very little attempt was made to standardise the products. Buyers almost invariably specified the retort method of testing, with the thermometer immersed in the liquid, and generally the condition of the market as regards specification and testing was most unsatisfactory. The control over benzol products exercised by the Ministry of Munitions brought about a great improvement. The side-tube flask was universally substituted for the old-fashioned retort, the grades of each spirit were standardised, and specifications were made more drastic. The reasons for this change were principally two; the urgent need for toluol early in the war and its consequent exclusion from benzol and solvent fractions; and secondly, the fact that the newly organised explosives factories required materials sufficiently pure to be used directly, whereas the makers of coal-tar dyes had been in the habit of purchasing the various commercial grades, which they themselves further rectified.

Typical pre-war products were sold under the following heads, the tests in every case being by the retort method:—

- 50/90 BENZOL, giving 50 per cent. at  $100^{\circ}$  C., 90 per cent. at  $120^{\circ}$  C.
- 90'S OR 90 PER CENT. BENZOL, with 90 per cent. distilling between  $80^{\circ}$  and  $100^{\circ}$  C.
- 90 PER CENT. TOLUOL, giving 90 per cent. between  $100^{\circ}$  and  $120^{\circ}$  C.
- 90 PER CENT. SOLVENT NAPHTHA, giving 90 per cent. from  $120^{\circ}$  to  $160^{\circ}$  C.

COMMERCIAL PURE BENZENE AND TOLUENE were required to give 95 per cent. distillate within a range of  $0.8^{\circ}\text{C}$ .

HEAVY NAPHTHA varied greatly according to requirements, but usually gave 90 per cent. between  $160^{\circ}$  and  $190^{\circ}\text{C}$ .

The 90 per cent. grades were marketed both washed and unwashed.

It will be seen that 90's benzol and 90's solvent naphtha conforming to the above specifications would contain appreciable quantities of toluene. When, therefore, the great shortage of toluene was realised in the earlier part of the war, the manufacture of these grades ceased. The sale of solvent naphtha containing more than 5 per cent. of toluene was stopped, and 90's benzol, which contains approximately 84 per cent. benzene, 15 per cent. toluene and 1 per cent. xylenes, was replaced by "Standard Benzol." This spirit, distilled in a side-tube flask with the thermometer in the vapour, was required to give at least 95 per cent. at  $90^{\circ}\text{C}$ . It contains approximately 96 per cent. of benzene and 4 per cent. of toluene.

The distilling range of solvent naphtha was altered to  $135^{\circ}$ — $160^{\circ}\text{C}$ ., and 90's toluol was required to give 90 per cent. between  $100^{\circ}$  and  $117^{\circ}\text{C}$ ., also by the flask method.

In the case of pure benzol and pure toluol, the distilling range was reduced from  $0.8^{\circ}$ — $0.5^{\circ}\text{C}$ ., the method of distillation being clearly laid down.

Although it is now possible to obtain any desired class of spirit, there is every indication that these improved standards will be wholly, or to a great extent, retained, and it may therefore be useful to give here the

### Government Specification for Pure Benzol

APPEARANCE.—To be a clear water-white liquid free from suspended solid matter.

SPECIFIC GRAVITY.—The specific gravity is to be not less than 0.883 and not more than 0.887 at  $15.5^{\circ}\text{C}$ .

BOILING POINT.—Must correspond approximately to  $80.5^{\circ}\text{C}$ . corrected.

SULPHURIC ACID TEST.—90 c.c. of the benzol shaken with 10 c.c. of 90 per cent. sulphuric acid for five minutes should impart only a slight colour in the acid layer.

### *Distillation Test*

APPARATUS.—A fractionating flask of 200-c.c. capacity fitted with thermometer graduated to read to one-tenth of a degree Centigrade and so adjusted that the top of the bulb is on a level with the side tube. The flask to be placed on a sheet of asbestos board having a hole 1 inch in diameter in the centre, in which the bottom of the flask rests, the bulb being surrounded by a cylinder of wire gauze resting on the asbestos sheet, and of such a height

that the top of the cylinder is on a level with the top of the bulb.

**DISTILLATION.**—100 c.c. of the benzol are placed in the fractionating flask and heated by a small flame on the portion of the flask exposed by the hole in the asbestos sheet, the distillation being conducted at such a rate that the distillate passes from the condenser into a 100-c.c. graduated cylinder at the rate of about 7 c.c. per minute. The temperature is read when 5 c.c. and again when 95 c.c. have collected in the receiving cylinder. The difference between the two readings must not be greater than  $0.5^{\circ}\text{C}$ .

### Government Specification for Pure Toluol

This specification is exactly similar to the foregoing, except that the limits of specific gravity are 0.868 and 0.870, and that the boiling point must correspond approximately to  $110^{\circ}\text{C}$ .

### Motor Spirit

Since the removal of the Government restrictions consequent upon the signing of the armistice, a great deal of attention has naturally been given to the production of a standard grade of benzol for use as motor fuel. The author will endeavour to deal with this important development in Chapter XVIII., but it is of interest here to notice the standard specification issued by the National Benzole Association. This provides that all benzol sold as motor spirit shall conform to the following requirements:—

- (1) **SPECIFIC GRAVITY:** 0.870 to 0.885.
- (2) **DISTILLATION TEST (*by Flask*):** Benzol shall give a distillate of not less than :
 

75 per cent.	at $100^{\circ}\text{C}$ .
90     ,,	at $120^{\circ}\text{C}$ .
100    ,,	at $125^{\circ}\text{C}$ .
- (3) **SULPHUR:** The total sulphur shall not exceed 0.40 per cent.
- (4) **WATER:** The benzol shall be entirely free from water.
- (5) **COLOUR:** Water-white.
- (6) **RECTIFICATION TEST:** 90 c.c. of the sample shaken with 10 c.c. of 90 per cent. sulphuric acid for five minutes shall not give more than a light brown colour to the acid layer.
- (7) **PURITY:** Benzol shall be entirely free from acids, alkalis and sulphuretted hydrogen.
- (8) **FREEZING:** Benzol shall not freeze until below  $7^{\circ}\text{F}$ . (25 degrees of frost).

Unfortunately this specification is, in the author's opinion, open to objection in one or two respects. Firstly, the lower limit of specific gravity, 0.870, excludes many benzols which would make excellent motor spirits in every way, but which have a lower specific gravity owing to a high content of paraffins. It is well known that the low-boiling paraffins do not detract from, but actually enhance, the qualities of a motor benzol, and it

should be noted that a mixture of 90 per cent. of benzene with only 10 per cent. of petrol—surely an efficient motor spirit!—would fall far outside the specified limits.

Provided there are sufficient low-boiling constituents present to allow of quick starting from the cold, there is no objection to a certain percentage of solvent naphtha being included in a motor benzol, and it would therefore be well to raise the final temperature of the distillation test.

Lastly as to sulphur—0.40 per cent. by weight represents only 153 grains of sulphur per gallon, whereas it has been stated on more than one occasion that benzol containing 240 grains of sulphur per gallon has been used successfully in motors. If the higher figure is a safe one, much extra expense in acid washing would be saved by its substitution for the figure specified.

The National Benzole Association, which is doing excellent work, is now only in its infancy, and, no doubt, experience will necessitate modifications in the standards set down.



## CHAPTER XI

### THE RECTIFICATION PROCESS

THE rectification of benzol comprises the purification of the crude spirit and its subsequent separation into the desired commercial products. This entails chemical washing and fractional distillation, which operations are almost invariably carried out intermittently. Various processes for continuous fractionation have been proposed and some are in more or less successful operation, as also are one or two installations for continuous washing. But the success of these methods depends on so many factors, such as uniformity of crude and of conditions, the plant entailed is relatively expensive, and so much skilled supervision is necessary that the intermittent method remains at once the more usual and certainly the more advantageous for the average gasworks.

The intermittent process varies slightly in method of application. Theoretically it might be possible to perform the whole process by fractionation alone, but in practice this is not the case. The chief reasons are : the presence of small quantities of a large number of impurities ; the proximity of the boiling points of some of these to the boiling points of the pure products ; the expensive nature of the drastic dephlegmation that would, therefore, be necessary ; and the formation of " constant boiling mixtures " of the benzene hydrocarbons with some of the impurities. The crude spirit is, therefore, washed with sulphuric acid which removes unsaturated compounds, olefines, dienes, etc., together with any pyridine and some sulphur compounds. This is followed by washes of water, dilute caustic soda, and again water, in order to free the benzol of the excess of sulphuric acid and any tar acids which may be present. The quantity of the latter in benzol from gas is, however, practically negligible.

Whilst the washing process does not vary much in application, the method of distillation differs considerably from works to works. Some workers apply the washing first of all to the crude benzol, whilst in other cases the crude is subjected to a preliminary distillation ; in fact, crude benzol is often separated into " crude fractions " before washing. There can be no doubt that preliminary distillation, which eliminates the creosote fraction, is always desirable, if only on the score of economy. In washing there is always a certain amount of loss of acid, which is unavoidable and which varies with the bulk of liquid dealt with.

The washing of the smaller quantity of distillate tends, therefore, to economy. Such a preliminary distillation is carried out in a "blow over" still provided with a short fractionating column, by means of steam. The unwashed crude fraction is quickly run until all the solvent naphtha comes over. The residue in the still consists of creosote, naphthalene, etc., and, after cooling out of the latter, may be returned to the wash-oil—from which it was originally derived.

An alternative method, and one which is becoming more popular, is to fractionate the benzol directly into forerunnings, and unwashed benzol, toluol, etc., fractions. These are washed separately, and finally refractionated. Each of these methods has its advantages, but the more suitable for the average gasworks, where the quantities of spirit handled are not great, is the preliminary distillation into one "unwashed benzol" fraction.

### Washing

The washing process is practically the same in application and results in each case. Olefines, dienes and other unsaturated compounds are removed by the acid, partly by polymerisation and resinification, and partly by solution in the acid. The acid used is moderately strong—usually of about 1.8 specific gravity—and a thick, dark brown residue is obtained known as "acid tar."

If it is desired to eliminate thiophene and thiotolene—an this is necessary when producing pure benzene, etc., for dye manufacture—a subsequent wash with concentrated acid is necessary. This effectively removes the sulphur compounds by sulphonation. On account of the costliness of this, and of the necessity for using excess of acid, various other processes for removing thiophene have been devised. Probably the most successful is that patented by Dutt and Hamer, in which the result is attained by chlorination. The calculated quantity of chlorine is used, either as a gas or dissolved in water, and the chloro-compound formed with the thiophene is of comparatively high boiling point, and therefore remains in the residue from the subsequent fractional distillation.

### Removal of Various Impurities

Carbon disulphide forms the chief constituent of the forerunnings, in which it occurs mixed with low-boiling paraffins and some benzene. For motor spirit these paraffins are a distinct advantage, but the disulphide is, of course, objectionable. Efforts have therefore been made to remove the latter impurity by chemical means. J. A. Wilson (*Gas World*, December 7th, 1918) has patented a process whereby this result is achieved. Forerunnings (or benzol) are washed, for two hours and at a temperature of 65°–68° C., with a 10 per cent. solution of caustic soda the washer being provided with a steam coil and agitator. The

carbon disulphide combines to form sodium thiocarbonate according to the following reaction :—



The spent wash-liquor is revived with lime or by other means, and is found more active after revivification than when new. The hydrocarbon is rewashed with this revived liquor, and 95 per cent. of the disulphide is removed. Since  $\text{CS}_2$  comprises about two-thirds of the total sulphur in crude benzol, and about 9 per cent. of the volume of forerunnings, the importance of such a method is obvious.

If there is any appreciable quantity of tar acids in the crude benzol, it may be found profitable to wash with dilute caustic before the acid wash in order to recover these, but such is not usually the case with benzol derived from coal-gas. In the case of large plants other economies are possible. Owing to the high cost of caustic soda compared with that of soda ash (commercial sodium carbonate) it is frequently much cheaper to manufacture the necessary caustic by the addition of lime to a solution of soda ash.

Acid tar is heated in various ways by steam. As a result there is obtained a dilute sulphuric acid which may be used in sulphate of ammonia manufacture, together with a hard, carbonaceous solid residue, which is much more easily disposed of than the original acid tar.

After washing, then, we are left with either one fraction of washed benzol, or with various washed "once-run" fractions of benzol, toluol, etc. These must now be refractionated, and the arrangement of the whole plant is shown diagrammatically in FIG. 53. The fractionating still is heated by means of closed steam coils, while the later stages of the operation are assisted by open steam. The vapours pass from the still, which is worked intermittently, through a fractionating column, and finally through an efficient water-cooled dephlegmator to the separator, whence they are taken to the various receiving tanks.

Reference has been made in Chapter II. to the process of fractional distillation and to the theories underlying it. It is sufficient to add that the washed once-run benzol is transferred from the washer, after all the water has settled out, into the final fractionating still. This still is provided with dry steam coils, open steam distribution and fractionating column, the last being followed by an efficient water-cooled dephlegmator. On heating the still a small quantity of forerunnings comes over, after which fractions may be run giving any desired range of pure products. It must be remembered that, although open steam is excluded until later in the operation, we have a mixture of vapours to deal with, and that in consequence the still-head temperature for giving, say, pure benzene, will not correspond strictly with the boiling point of benzene. For similar reasons

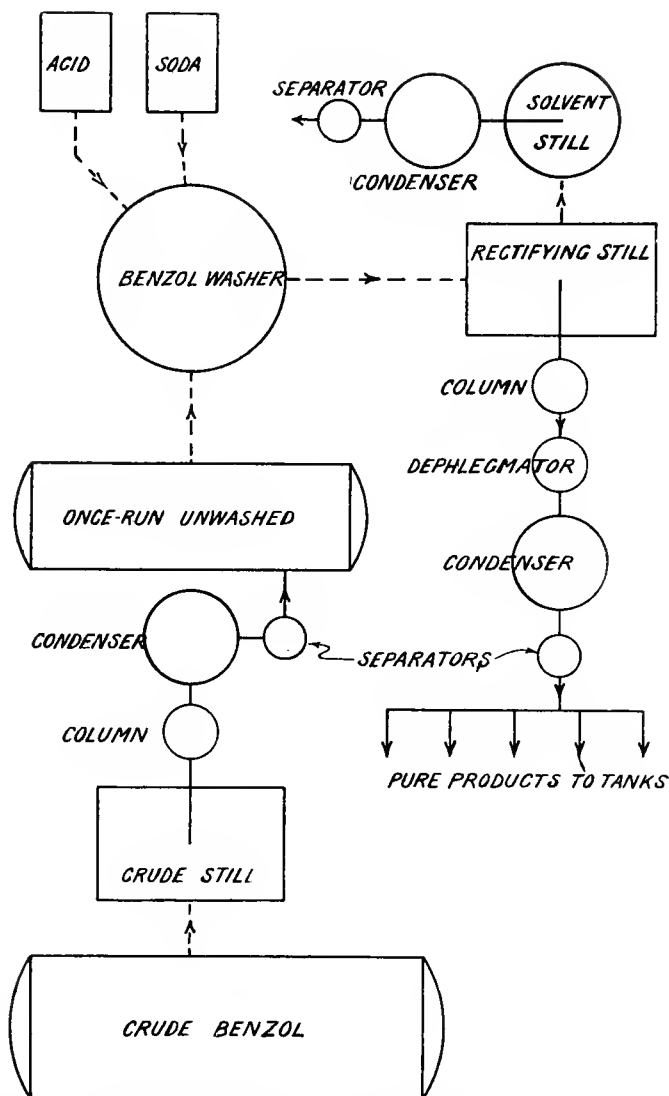


FIG. 53.—DIAGRAMMATIC PLAN OF BENZOL RECTIFICATION PLANT.

it is impossible to get absolute separation of the various hydrocarbons; but a close approximation may be reached by very drastic cooling in the dephlegmator. The quality of the product coming over at any particular time cannot be found by reading

the still-head thermometer, and the operation is therefore controlled by frequent chemical tests of the liquid leaving the end of the condenser. Experience will indicate suitable "cut-points" at which to change over from the various fractions required.

### Paraffins

The presence of paraffins frequently causes complications at this stage of the rectification. These bodies are not removed by any washing process, and moreover have boiling points extending over the range of the benzene series—in some cases very near to those of the pure benzols. To eliminate as much paraffin as possible a process of "sweating out" must be adopted, consisting of a slow rate of distillation coupled with very drastic

TABLE 25.—YIELD OF RECTIFIED PRODUCTS FROM CRUDE BENZOL.

Average strength of crude benzol (retort test).	Percentage once-run benzol produced.	Percentage acid used in washing (by weight).	Percentage total loss.	Percentage loss in washing.	PERCENTAGE OF PRODUCTS.				
					95 per cent. benzol.	85 per cent. toluol.	Solvent naphtha.	Creosote and residue.	Naphthalene salts.
45 per cent. at 120° C.	75	4	8	7	32	16	13	21	10
60     "     "	84	6	11	9	45	16	8	14	6
62     "     "	85	3	7	6	45	17	8	16	7
65     "     "	87	7	10	8	55	6	8	17	4

dephlegmation. Some benzol, of course, comes over with the paraffins under the best conditions, but the trouble does not end there. For certain members of the paraffin series form "mixtures of constant boiling point" with the benzenes. Young in his book on *Fractional Distillation* gives several examples of such mixtures including one of normal hexane and benzene, in which case "no amount of fractionation with the most perfect apparatus would make it possible to separate either pure normal hexane or pure benzene from the mixture . . . because the boiling points of the hexane and of the binary mixture differ, in all probability, by less than 0.1°." It is, therefore, practically impossible to produce by fractionation uncontaminated benzene or toluene from a paraffinoid crude. The presence of paraffins is immaterial when the rectified product is to be used as a motor fuel, but when benzene, toluene, etc., are required for other purposes, such as the manufacture of dyes and explosives, a limit to the paraffin content is usually specified. In such cases the

product after rectification can only be rendered suitable by admixture with a sufficient proportion of paraffin-free hydrocarbon.

The rectification process naturally entails some loss in volume of the liquid, and this varies from 8 to 15 per cent. ; about two-thirds of this quantity being due to the operations of washing, and the remainder lost during distillation.

#### Yield of Products

The yield of rectified products obtained (as well as the amount of loss) varies considerably with the character of the crude benzol, but the useful table on p. 141, due to Hamer, gives a very good indication of the average yield of products. '

## CHAPTER XII

### THE RECTIFICATION PLANT

A DIAGRAMMATIC plan of a benzol rectification plant has been given in FIG. 53, and this indicates a suitable general arrangement, in the lay-out of which attention should be given to convenience in handling the various fractions and other liquids. Advantage should be taken of differences in level, etc. ; and the plant must be suitably housed, chiefly in order to protect fractionating columns and dephlegmators from draughts.

Many of the points discussed in Chapters IV. and V. apply equally to crude benzol and rectification plants, and in particular every precaution should be taken to ensure good joints throughout the plant. Tanks and other plate-work should be strongly riveted and well caulked. Storage tanks should not be elevated if it can possibly be avoided, but should be placed in pits in the ground. Various portions of the plant will now be discussed—this is somewhat difficult owing to the great diversity of design and to the fact that many are the subjects of patents—and finally one or two typical installations will be described.

#### Blow-over Still

In this vessel the preliminary separation of the crude product is carried out. In its usual form this still consists of a horizontal cylinder of mild steel plates,  $\frac{3}{8}$  in. thick, with strongly riveted and stayed ends. The capacity of the cylinder varies from 2,000 to 4,000 gallons, and a charge represents about half to two-thirds of this capacity. A cast-iron steam chest is bolted to each end of the still, and these are connected by 1 or 2-inch tubes expanded into the end-plates. A perforated pipe along the bottom supplies "open" steam, and the still is surmounted by a fractionating column, usually of the perforated tray type. The condensates from this column are returned to the lower part of the still, and priming is prevented by a baffle chamber through which the vapours pass after leaving the still and before entering the column. This chamber may form the base of the column itself, or may be placed separately alongside the latter. Such a blow-over still is shown in FIG. 58 (p. 152) as the "primary still." It carries the usual mountings which must include a pressure gauge and safety valve.

### The Benzol Washer

Washers may vary greatly in design, though very little in principle. A typical washer consists of a vertical cylinder of cast-iron or mild steel with a conical bottom, the capacity of the whole being from 2,000 to 4,000 gallons (or less, according to the volume of unwashed once-run benzol to be dealt with). The washer should be covered with a cast-iron or wooden top, having an inspection lid, and may be lead lined. Lead-lined washers are preferred, although all the corrosion having been noted to

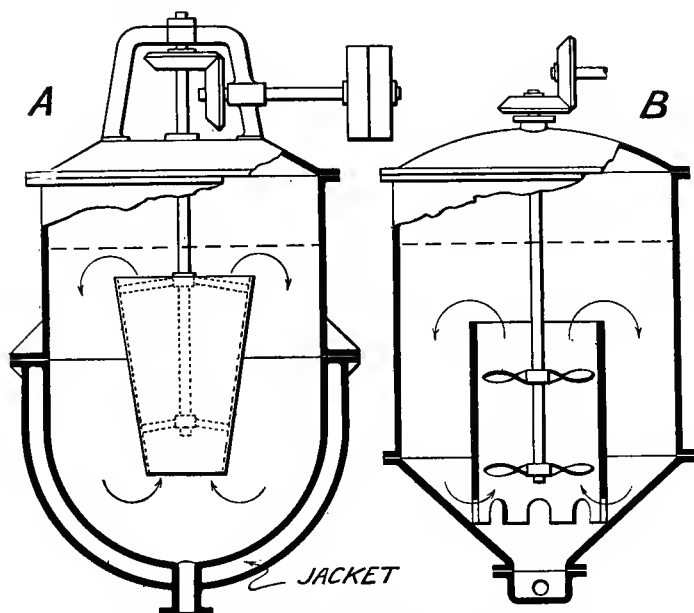


FIG. 54.—BENZOL WASHERS OR AGITATORS.

- (A) With Cone and Water Jacket.  
(B) With Sleeve and "Propellers."

occur on the conical portion of unlined washers, it has been suggested that this portion only need be lined. In the case of cast-iron vessels it is doubtful if lead lining is either necessary or advisable.

In the case of very small washers the agitation of the contents may be performed by stirring with a stout wooden rod, but larger vessels are fitted with mechanical agitators. These are commonly driven by bevel gearing operating a central shaft, upon which is suspended, in one of the best forms, a hollow truncated cone. This is rotated at about 120 revolutions per minute and centrifugal



force sets up currents through the cone, an example of the use of which is shown in FIG. 54, A. The cone is frequently replaced by an Archimedeian screw working in a cylinder, through which it raises the liquid. In other cases screw "propellers" are used as in FIG. 54, B. Impure benzols sometimes become considerably heated during acid washing, and for this reason the lower portions of washers are at times fitted with cold-water jackets as indicated in FIG. 54, A.

The top of the washer is fitted with a benzol charge pipe,

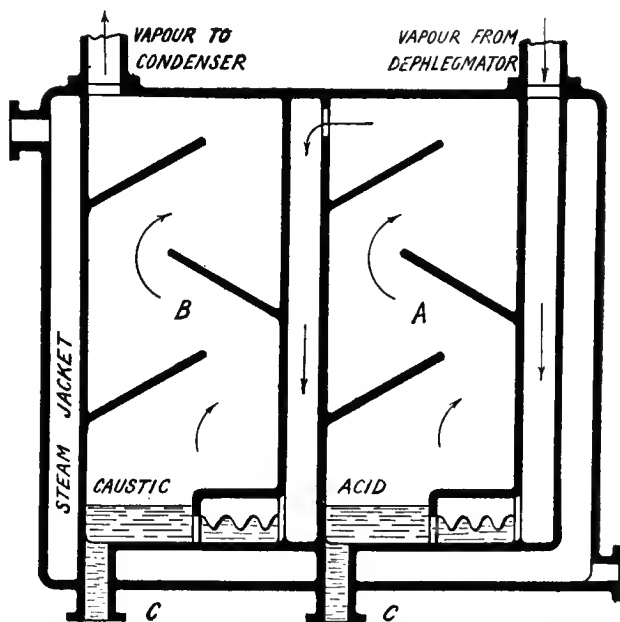


FIG. 55.—SIMON CARVES' APPARATUS FOR CONTINUOUS WASHING OF BENZOL VAPOURS.

inlets for acid and soda, and a water connection equipped with a length of flexible hose.

At the lowest point of the washer a cast-iron tee is bolted, the two free flanges of which are fitted with large bore plug-cocks. These cocks (the plugs of which should be cleaned and greased frequently) serve to discharge acid tar, spent soda, water, etc., and washed benzol respectively. The latter cock is permanently connected to the washed spirit receivers or to the final rectifying still, and the former opens into a lead-lined wooden trough which serves to conduct the spent liquids away, and also facilitates inspection of the liquid leaving the washer.

The benzol washer should be situated in a separate building, and if the agitator be electrically driven, the starter-box, fuses, etc., in connection with the motor should be of the totally enclosed type, and placed as far from the washer as is practicable, preferably in a separate building; the reason for this is to minimise the risk of fires from sparking.

### Continuous Washing

It has been suggested on several occasions that continuous washing of the benzol, either as liquid or vapour, should be incorporated with the distillation process. These suggestions have not been acted upon to any great extent owing to the complicated

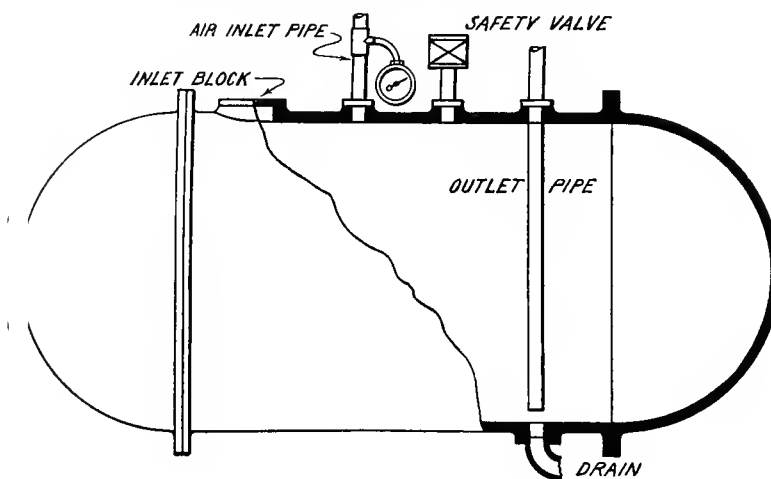


FIG. 56.—CAST-IRON ACID EGG.

nature of the necessary apparatus, and to the need for careful skilled supervision. The future, however, will probably see big improvements in this direction, and the plant patented in 1915 by Messrs. Simon Carves is worthy of note. This is shown in FIG. 55.

It consists of two compartments A, B, each containing a bubbling hood, baffle plates, and passages and overflows for the vapours and liquids. The vapours are taken from the dephlegmator and passed through acid in A, afterwards rising between baffle plates which serve to entrap any acid spray. In a similar manner soda washing is effected in B, whence the vapours pass to the condenser. The acid and soda are renewed from time to time by means of suitable inlet pipes (not shown), and the spent liquids leave at C, C. In order to prevent condensation the washer is steam

jacketed, and a partial vacuum is usually maintained at the outlet to overcome the back pressure thrown by the apparatus.

### Acid and Soda Tanks, etc.

Acid tanks must be lead lined ; those for caustic may be of wrought iron or mild steel, and the first caustic tank is that in which the solution is prepared (where caustic is made from soda ash and lime other tanks for mixing, settling, etc., are needed). Acid and caustic solution are run into " eggs "—pressure vessels of cast iron, oval in section (FIG. 56)—and blown by means of compressed air into measuring tanks. The latter have a capacity of 300—500 gallons each, and are placed at such a level that the liquids will flow into the washer by gravity. They are provided with floats, gauges or other indicators, graduated in gallons, by which the volume of each liquid admitted to the washer may be directly ascertained. Lead pipes, of  $\frac{3}{4}$  or 1-inch diameter, extend from these measuring tanks through the cover of the washer, and the flow of each liquid is controlled by a cock—which, in the case of the caustic tank, should be placed as near to the latter as possible in order to obviate the blockage of the pipe.

### Fractionating Stills and Columns

The still in which the final fractionation is performed is of very similar construction to the blow-over still. It comprises a horizontally placed steel cylinder, steam chests and tubes, and open steam spray, but is surmounted by a much more efficient column than that of the primary still. The vapours furthermore pass through a dephlegmator placed between the outlet of this column and the inlet to the condenser.

The capacity of the still suffices for a charge of from 2,000 to 4,000 gallons of washed once-run benzol. The liquid is heated by " closed " steam, the vapours passing either direct or through a baffle chamber into the base of the fractionating column, which is the most important part of this apparatus. The dimensions and design of fractionating columns vary considerably, and those for a plant of average size usually belong to one of the following types :—

(a) A tower, some 3 feet in diameter, and 20 feet high, composed of eighteen to twenty cast-iron bubbling tray sections. Each section is fitted with a number of serrated bubbling hoods and an overflow pipe to maintain the level of the liquid, the general arrangement being as shown in FIG. 23 (p. 68).

(b) A column 2 feet 6 inches to 3 feet in diameter and from 20 to 30 feet high, built of mild steel plates, and divided at vertical intervals of 8 or 10 inches by perforated steel plates. The plates contain preferably a large number of small perforations,

and each section is fitted with an overflow pipe sealed in a recess in the plate next below—*see* columns in FIG. 58 (p. 152).

(c) A plain cast-iron or steel tower packed with mild steel or earthenware Raschig rings.

Whilst either of the types (a) or (b) forms an efficient fractionating column, there is little doubt that type (c)—the Raschig ring column—is the most efficient. These rings are commonly 1 inch in diameter by 1 inch long and may be obtained in iron or in glazed or unglazed earthenware, the unglazed ring being usually preferred. Much less back pressure is thrown by a column of these rings, owing to their relatively small volume per unit of surface area, although the character of the ring packing breaks up the stream of vapour very effectively, and gives an excellent “scrubbing” action to the condensed liquids. On this account a column of this type may be much smaller than a tower of bubbling trays or perforated plates, and yet be more efficient. The chief disadvantage in connection with Raschig rings is their first cost per cubic foot of column space. One cubic foot requires 1,200 earthenware rings (1 × 1 inch), and these weigh 27 lbs. Such a ring will withstand a pressure of 45 lbs. at its weakest point (along the diameter) and 2 or 3 tons longitudinally.

Columns packed with Raschig rings are more efficient than other types, but appear to be rather more sensitive and susceptible to draughts.

In the design of perforated plate or of bubbling-hood columns it must be remembered that their capacity is largely limited by the size of the overflow passages, and these must therefore be provided of ample dimensions.

### Dephlegmators

After leaving the fractionating column the benzol vapours pass downwards through the dephlegmator, which is in effect a water-cooled reflux condenser, the severity of the condensation being controlled by varying the water supply. Probably the best type of dephlegmator is that designed on the lines of the tubular condenser (FIG. 25, p. 70); the cooling water passes through a number of vertical steel tubes around which the vapours circulate. Such a dephlegmator is shown in FIG. 58 (p. 152). The condensates are taken from the bottom of the vapour space and returned to the top section of the fractionating column. The character of these condensates determines very largely the quality of the distillate, and this is accordingly controlled by increasing or decreasing the supply of water. This may be effected by one cock on the water supply, or preferably by a series of three water outlet cocks fixed at different levels in the top half of the dephlegmator, the water entering at the bottom.

The importance of the dephlegmator or analyser as it is sometimes called, has been shown by J. A. Wilson, and his results are

given in *Table 26*. Three charges of washed once-run benzol were distilled with the analyser in operation, followed by three charges distilled with the analyser by-passed.

TABLE 26.—EFFECT OF USING ANALYSER.

FRACTION.	THREE CHARGES WITH ANALYSER.	THREE CHARGES WITHOUT ANALYSER.
Benzol as charged.	Drop, 79.6° C. Dry, 99.5° C.	Drop, 78.7° C. Dry, 101° C.
	Gallons.	Gallons.
Total forerunnings . . . . .	960	1,106
Pure benzol . . . . .	9,101	8,718
To re-work . . . . .	516	746
90's toluol . . . . .	156	195
Percentage pure benzol in total distillates . . . . .	84.75	81.10

The water required for dephlegmation varies from 2 to 3 gallons per gallon of pure products made, but this often includes the waste water from the condenser.

### Condensers and Separators

These have been fully described and illustrated in Chapter IV. The water required for condensation on an average rectifying plant is about 2 gallons per gallon of pure products.

### Storage Tanks

These have been described in Chapter IV. in connection with the debenzolising plant, and the same remarks apply here. The number of tanks required on the rectification plant varies, however, with the method adopted. In the case of the average gasworks, where the whole crude is "blown over" into a single unwashed fraction and this subsequently washed and fractionated, tanks are required for the following fractions:—

- (a) Once-run unwashed benzol,
- (b) Forerunnings,
- (c) Pure benzol,
- (d) Intermediates,
- (e) Pure toluol,
- (f) Intermediates,
- (g) Residues (for solvent),
- (h) Solvent naphtha,
- (i) Naphthalene pans for "bottoms,"

making eight tanks in all, the capacity required for each being easily found from local conditions. In the larger plants a separate solvent naphtha still is provided and this may eliminate tank (g), since the residues from the fractionating still are then run directly into this extra still. It is, however, advisable to include tank (g) in any case so that, if desired, both rectifying and solvent stills may be worked at the same time.

If the crude is subjected to a preliminary fractionation before washing (*i.e.*, into unwashed benzol, toluol and solvent) three tanks for these fractions must be substituted for tank (a). The total storage necessary will then be eleven tanks, or ten if a solvent naphtha still is installed, in addition to the naphthalene pans.

It is always advisable to have one or two spare tanks near the plant in case of emergency, or in the event of a call for special fractions.

### Accessory Plant

All connections must be made with good sound joints, and plenty of steam and water (the former at a pressure of at least 90 lbs. per square inch) must be provided for.

As regards pumps, any reliable type may be used, and gun-metal valves may be fitted where pure products have to be handled.

Thermometers should be fitted in the bases of stills and at the outlets of fractionating columns and dephlegmators. These, however, are, perhaps, not strictly necessary, since, as explained previously, their readings give no reliable indication of the character of the fractions coming over.

The main features of a few typical plants for the rectification of benzol will now be described.

### Typical Rectification Plants

#### *The Chemical Engineering Co.'s Plant.*

A very suitable form of rectification plant for the average gasworks is that made by the Chemical Engineering Co., and illustrated in FIG. 57, from which the tanks and pumps are omitted.

Crude benzol is distilled in the primary still H, the once-run benzol condensing in K and running through the separator L to its storage tank. From here a charge is pumped periodically into the washer A, and after being suitably washed and allowed to settle, the purified once-run spirit is allowed to flow directly into the fractionating still B, which is fitted with a column C and water-cooled dephlegmator D. The latter is of high efficiency, with the result that the products leaving the separator

F are pures. The acid eggs E are worked by the air compressor, P.

In this case the fractionating column is of either the perforated

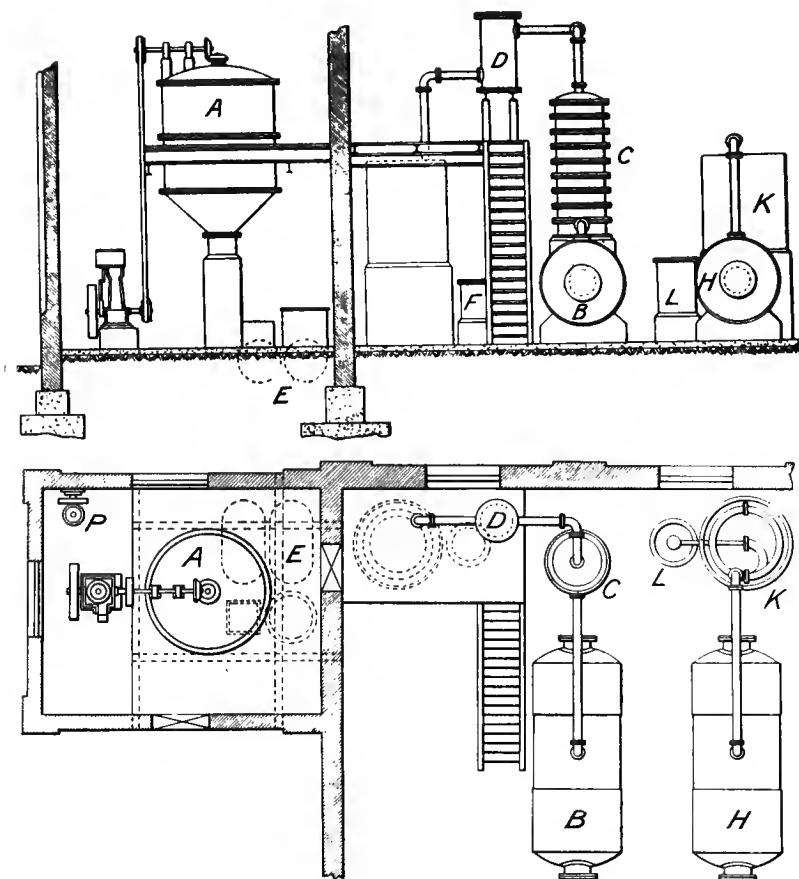


FIG. 57.—CHEMICAL ENGINEERING CO.'S PLANT FOR BENZOL RECTIFICATION.

plate or the bubbling-tray type, and the dephlegmator is tubular. The condensers are both built up of cast-iron segments, as illustrated in FIG. 26 (p. 70).

### *R. and J. Dempster's Plant*

A feature of this plant is the fact that fractionating columns are provided for both the primary and final fractionating stills,

and the columns are composed of perforated plates fitted with sealed overflow pipes. FIG. 58, illustrating both stills, indicates clearly the construction of these, and also of the body of the still, steam chests, etc. In this case both condenser and dephlegmator (or "analyser") are tubular, and as they contain a large

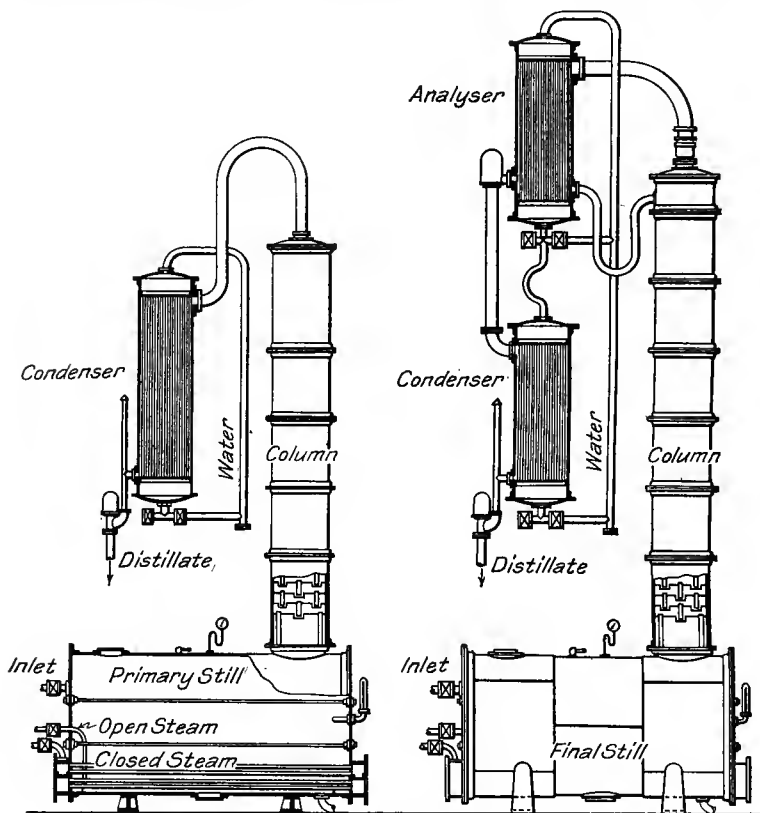


FIG. 58.—PRIMARY AND FINAL FRACTIONATING STILLS.  
(R. and J. Dempster, Ltd.)

number of tubes of comparatively small diameter are very efficient. The efficiency of the analyser, and the provision of a column on the primary still tend to greater purity of the products.

#### *Simon Carves' Combined Plant*

A plant of novel design, and presenting many very good points is shown in FIG. 59. The object in view here is, at one operation,



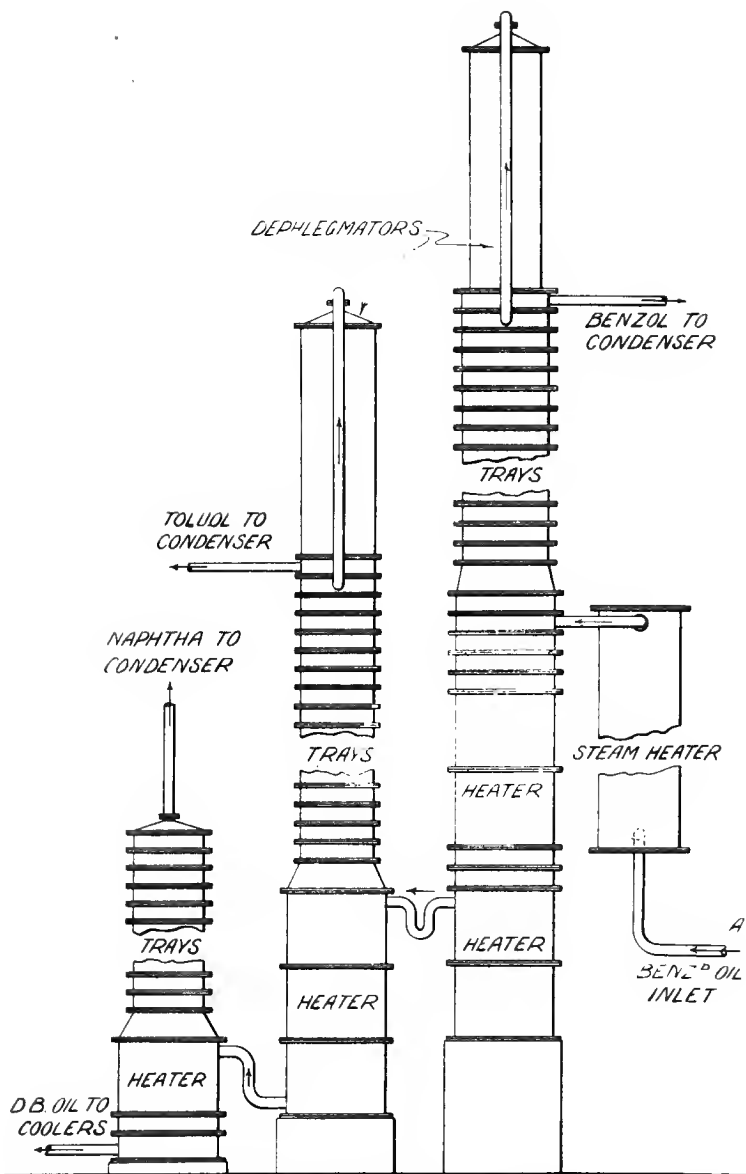


FIG. 59.—SIMON CARVES' COMBINED DEBENZOLISING AND RECTIFYING PLANT.

to debenzolise the wash-oil and produce directly once-run benzol, toluol and solvent naphtha. Benzolised oil enters the plant at A, and after passing through a steam preheater enters one tray of a column still. The latter comprises several bubbling-hood trays and two reheating chambers, the whole being surmounted by a tray-type fractionating column and water-cooled dephlegmator. Fractionation here is so drastic that the vapours passing away condense directly to once-run (unwashed) benzol, which of course contains also the forerunnings. The partially stripped

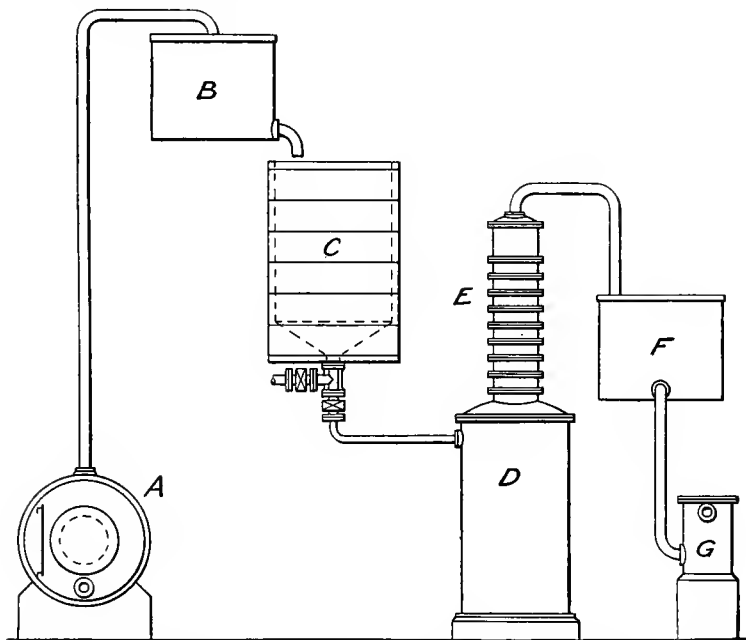


FIG. 60.—SMALL SCALE RECTIFICATION PLANT FOR PRODUCTION OF MOTOR SPIRIT.

oil, containing all the solvent naphtha and about 90 per cent. of the toluol, passes into a second column still, similar to the first, but in which the fractionation is less drastic. This still has its own dephlegmator and condenser from which once-run toluol is obtained. By passing the oil through a third still, equipped with a shorter column but having no dephlegmator, once-run solvent naphtha is similarly produced. The wash-oil leaving the third still is now completely debenzolised, and if sufficient open steam has been used in the various distillations it should be practically free from naphthalene. The use of reheating

chambers (as described in Chapter IV. in connection with this firm's debenzolising plant) serves to maintain the desired temperature in each still, and also ensures a low percentage of water in the debenzolised oil.

The reader will possibly be acquainted with rectifying apparatus on a much larger scale than the foregoing, and many such installations are working to-day. The present aim, however, is to give a general idea of the type of plant most suitable for use in gasworks. In general, the very large plants differ from these only in the size and number of units. Thus one undertaking may have a fractionating still for the production of 90's benzol and toluol, with an additional unit for working these up into pure products. And most of the larger plants will include a separate still for solvent naphtha.

### Plant for Production of Motor Spirit

The installations just described are suitable for gasworks of average or larger size, and are designed for the production of pure products. For smaller works, or where the aim is the production of motor spirit only, a simpler and smaller type of apparatus is all that is necessary. Such is the motor spirit plant of the Chemical Engineering Co., which is illustrated in FIG. 60. This is merely a small-scale copy of the larger plant shown in FIG. 57, with two or three modifications. The usual primary still and condenser serve for the production of the once-run crude, but the rectification still is placed vertically, and sufficient fractionation is obtained in the trays of the column to render a dephlegmator unnecessary. The benzol washer, being of small capacity, contains no mechanical agitator, the operation being performed by hand with a wooden pole. This compact little plant is guaranteed to produce a spirit which will conform to the motor fuel specification of the National Benzole Association.

## CHAPTER XIII

### OPERATION AND CONTROL OF THE RECTIFICATION PLANT

As previously stated, the process of benzol rectification is carried on in a variety of ways at different works, though the fundamental principles remain the same. The differences chiefly lie in the order in which the operations are performed. The three most usual methods are :—

- (a) The crude benzol is washed with acid, caustic soda and water, and the washed crude is directly fractionated into the desired products.
- (b) The crude benzol is first subjected to a preliminary distillation into once-run unwashed crude, this fraction then being washed and subsequently refractionated.
- (c) The preliminary distillation is so conducted as to produce unwashed fractions, *i.e.*, unwashed once-run benzol, toluol, etc., and these fractions are separately washed and redistilled.

Method (a) is unsuitable in many ways. Firstly, it tends to waste of acid since there is no useful object in removing unsaturated bodies from residues which will afterwards be discarded. Moreover these residues are rendered useless—they cannot be returned to the wash-oil storage. The reason for this is the fact that some of the unsaturated impurities are removed by the acid by resinification, and the resulting resins dissolve in the washed benzol; being of high boiling point they remain in, and so contaminate, the residue from the final distillation.

Method (c) is the most modern, and, for large installations, undoubtedly the most economical mode of procedure. But a larger number of storage tanks and also, usually, of stills, is required and more supervision is entailed.

It may therefore be concluded that the second method, (b), is the most suitable for the operation of a rectifying plant on a gas-works, where the production of benzol is not usually of large quantity, and where, owing to benzol being a side issue, the plant is required to be not only efficient, but also as simple as possible in operation.

The process of rectification, therefore, will here be described as carried out by this method, and it is hoped that the details of procedure, etc., will enable the description readily to be applied to other cases.

### Preliminary Distillation

A charge of well-settled crude benzol is introduced into the primary or "blow-over" still and steam is turned on. The distillation is continued fairly rapidly, the outlet of the separator being connected to the once-run unwashed benzol storage. No open steam is necessary during the initial stages, but a good pressure of steam in the steam-chests is advisable. Forerunnings containing carbon bisulphide, light paraffins and benzene, come over first and the distillation is continued through the benzene, toluene and solvent naphtha stages, one fraction only being collected. The distillate is tested frequently during the later stages of the process by boiling in a side-tube flask, and when its "drop point" reaches a predetermined temperature—found from experience, and usually from  $140^{\circ}$  to  $150^{\circ}$  C.—the distillation is stopped. The residuc in the still is run out into cooling pans, where most of the naphthalene crystallises on cooling, the supernatant oil being returned to the wash-oil tank. It will usually be found advantageous to introduce live steam from a drop point of about  $120^{\circ}$  C. to the end of the fractionation.

### Washing

When the accumulation of once-run crude represents a sufficient volume, the benzol washer is charged with this liquid, which is allowed to settle thoroughly, and the last traces of water drawn off at the bottom. The agitator is then started and the spirit washed successively with acid, soda and water. Here again practice varies greatly with the ideas of the management and with the character of the unwashed crude. In any case the latter is first tested in the laboratory in order to find the proportion of sulphuric acid required. This varies from 4 to 10 per cent. of the volume of the benzol, and we will assume for purposes of illustration a figure of 6 per cent. The best method of procedure will then be as follows :—

Agitation of the benzol is begun and 2 per cent. of its volume of moderately strong sulphuric acid, say,  $144^{\circ}$  Twaddell, is gradually introduced from the acid-measuring tank. Agitation is continued for from half to one hour, after which the contents of the washer are allowed to settle for a further twenty minutes. The acid will have combined with some of the impurities to form a thick reddish-brown substance known as "acid tar." This is carefully run off from the conical base of the washer and the same process repeated with  $1\frac{1}{2}$  per cent. of acid of the same strength. Two washes follow with strong acid of  $160^{\circ}$  Twaddell, say, one of  $1\frac{1}{2}$  per cent. and one of 1 per cent., the process being exactly similar, except that the strong acid must never be allowed more than ten minutes in which to settle out.

After the removal of the last portion of spent acid the spirit

is carefully washed by allowing a shower of water to fall through it and down the sides of the vessel from a hose. This must be done without agitation and as carefully as possible. The bulk of the wash-water settles out quickly and is run off. Whilst the remainder is settling out a sample of the spirit is taken to the laboratory and tested as described in Chapter X. (p. 133) to find whether the acid washing has been sufficient. If not, a further quantity of acid must be used, care being taken that all water is previously removed from the washer. When the test shows that the acid wash has been complete the spirit is again washed with water agitating gently for twenty minutes. The water is allowed to settle and is removed, after which the excess of acid is extracted by washing the benzol with 1 per cent. of its volume of caustic soda solution (specific gravity 1.08—1.1) agitating for half an hour. This is followed by a final wash with water and prolonged settling. After the removal of all traces of water the washed crude benzol is run or pumped directly into the final rectifying still.

The removal of sulphur compounds by chemical means is not at present usual, though two methods for this have already been described. If either of these is in use it may be conveniently applied at this point. If the chlorination process (p. 138) be adopted, it must not be carried out until after a preliminary distillation has removed the wash-oil residue. This is due to the high-boiling chloro-compounds remaining in the residue, and for the same reason chlorination must always precede the final distillation.

### Final Rectification

The rectifying still being charged, steam is turned on to the heating coils, and water to the dephlegmator and condenser, the separator being put into communication with the fore-runnings tank. If no chemical removal of carbon bisulphide has taken place, this compound will very soon appear at the condenser outlet, in admixture with any low-boiling paraffins which may be present. The percentage of these substances existing in the crude spirit will give some indication of the amount of fore-runnings to be taken off, but this cannot be altogether relied upon since the latter always contains a certain proportion of benzene. In general, the preliminary fraction is run until the distillate gives a drop point of about 65° or 70° C. At this juncture the separator outlet is switched over to the rectified benzol tank and the supply of steam to the closed coil is increased, when the benzene fraction may be run at a fair rate. It must be noted that no open steam is used in these portions of the process, and that a plentiful supply of water to the dephlegmator is necessary. The action of the dephlegmator should be sufficiently drastic to return to the still from three to four times the volume of distillate actually being obtained. By the selective action

of this piece of apparatus only is it possible to ensure products of a suitable degree of purity.

The usual products aimed at in this rectification are 90 per cent. benzol, toluol, etc. When "commercial pures" are required it is rarely found to be economical—or even possible—to produce these direct. The 90's grades are therefore usually made and, when necessary, further rectified. Thus the large dyeworks are usually found to purchase 90's benzol and toluol, and to further refine these spirits themselves.

When making 90's benzol this fraction is collected until the distillate gives a first drop at about  $90^{\circ}$ — $95^{\circ}$  C., but if standard benzol is the objective the fractionation is not carried quite so far, say to  $85^{\circ}$  C.

Both theory and practice show us that it is not possible to turn over the delivery from benzol to toluol direct, and from a consideration of vapour pressures, etc., one would expect at this stage to obtain from the condenser a mixture of benzene and toluene. Such is the case, and therefore an "intermediate" fraction must first be taken off. The intermediates are sometimes stored separately, but are usually run back to the washed once-run crude tank—in any case they must subsequently be re-worked.

The intermediate or benzene-toluene fraction corresponds with a rise in drop point of  $10^{\circ}$  or  $15^{\circ}$  C., and when the latter reaches about  $100^{\circ}$  C. the collection of the toluol fraction begins. If the product aimed at be, as usual, 90's toluol the next cut-point occurs at about  $112^{\circ}$ — $115^{\circ}$  C. drop, and after that point various grades of naphthas are run. It will be found advisable soon after this cut to admit a small quantity of open steam to the still, and subsequent cut points will, of course, vary with the grade of naphtha desired. If the present-day quality of rectified solvent naphtha be aimed at, a small toluene-xylene or intermediate fraction must be run, and the solvent fraction is then collected between drop points of approximately  $130^{\circ}$  C. and  $160^{\circ}$  C.; the distillate from the latter temperature to about  $190^{\circ}$  C. being classed as heavy naphtha. Very little of the last fraction can be expected if a preliminary distillation has been made, and, in fact, the quantity of solvent naphtha in the charge is rarely sufficient to pass satisfactorily the column and dephlegmator. One means of overcoming this difficulty is to fit a by-pass connection to the apparatus whereby the naphtha vapours may be led direct from the still to the condenser. Frequently a separate still—without both column and analyser—is provided, and in this case the rectification is stopped after the toluol cut-point. The residue is then transferred direct to the solvent still, which is not worked until a full charge has accumulated from several distillations.

Analogous to this is the process known as "topping up." A complete benzol fraction, for instance, is run and then, instead of proceeding with the distillation of toluol, the still is allowed to

cool a little, and a fresh charge is made up by the addition of washed once-run spirit. This is continued until practically a full charge remains, from which intermediates and toluol are distilled. Some saving of time and plant is thereby effected, and "topping up" is frequently made use of in the primary distillation.

The disposal of the residue from the distillation of solvent and heavy naphtha is sometimes a source of trouble. Several methods for utilising this residue have been proposed and some will be discussed later, but if one of these is not in operation the residue must be discarded. On no account may it be returned to the wash-oil, for it contains the viscous, high-boiling resins produced by the action of sulphuric acid on the olefines, dienes, and other unsaturated hydrocarbons which are polymerised by it.

### Production of Motor Spirit

The above scheme for the rectification of benzol is applicable to the production of the usual commercial pure products, but the details such as cut-points, must be varied to suit particular requirements and for the production of special grades of spirit. A special grade of great importance is motor benzol, the standard specification for which has been given in Chapter X. In this case special regard must be had to the washing process, and an additional wash of 2 per cent. of concentrated sulphuric acid should be carried out in order to extract as much sulphur as possible in the form of thiophene. The carbon disulphide will, of course, remain unaffected by the washing process (unless the special processes are adopted to this end). In consequence, great care must be exercised in taking off the "fronts" or forerunnings. This portion of the second distillation should proceed very slowly and with very drastic dephlegmation in order to eliminate as much  $\text{CS}_2$  as possible. If these precautions be taken, little trouble should be experienced in the production of a motor spirit containing not more than the specified quantity of sulphur.

As regards the distillation of the washed crude, this will proceed as described above, except, of course, that only one fraction will be collected between the forerunnings and the heavy naphtha. In other words, the resulting motor spirit will contain all the benzene and toluene and some of the xylenes. The final cut-point for the motor benzol fraction will occur when the distillate "drops" at about  $130^{\circ}$ — $135^{\circ}$  C.

### Use of Vacuum

It has been remarked that the distillation of the solvent and heavy naphtha is assisted by the use of open steam. Some workers apply a partial vacuum to the plant at this stage, the



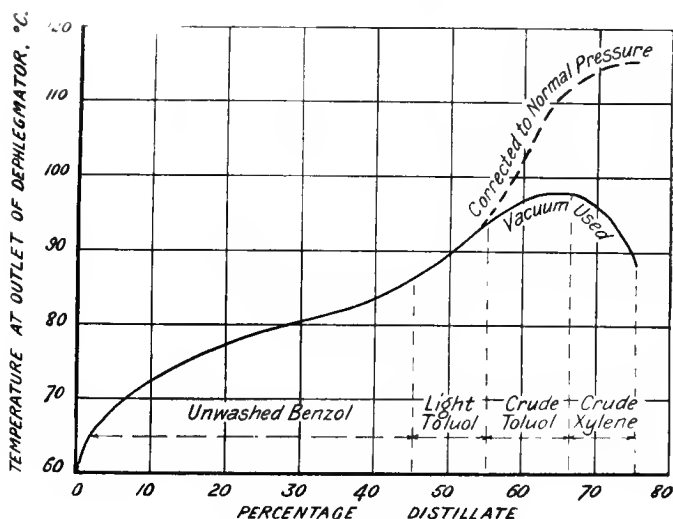


FIG. 61.—FRACTIONATION OF CRUDE BENZOL.  
(T. H. Butler.)

effect being to reduce the boiling points of the various constituents, and so further to assist the distillation. The extent of this reduction is shown clearly in an instructive curve given by T. H. Butler (FIG. 61).

### Continuous Rectification

A number of suggestions and designs have been put forward with the object of rendering the fractionation of crude benzol a continuous process, as distinct from the otherwise universal intermittent distillation above described. These types of plant are invariably composed of a number of stills in series, on the general lines of the combined plant illustrated in FIG. 59 (p. 153). Such installations are more or less still in the experimental stage, and as they are only suitable for the largest productions and, moreover, entail a considerable amount of skilled attention, they will not now be discussed.

### Control of Rectification

Since no open steam is used during the running of the benzene and toluene fractions, it would theoretically be possible to control the distillation and quality of the distillates, by the observed temperature of the vapours leaving the dephlegmator. This is not the case in practice, however, owing to the presence of small

quantities of paraffins and similar bodies, to the practical difficulty of leaky steam coils—always present to a greater or less extent—and to other factors. For this reason it is necessary to exercise very careful control, and although many systems are in use, the most usual is the frequent testing of the distillate leaving the condenser. The cut points are then found from the drop point and distilling range of the product. These tests must be comparative, and must therefore be performed under standardised conditions, using, of course, a side tube flask with the bulb of the thermometer placed immediately below the tube.

On some plants a different method is adopted, and the whole distillate is run into 40-gallon drums instead of into the storage tanks. The drums are numbered in rotation, and at the end of the distillation their contents are analysed, the desired final products then being obtained by suitable mixing. This method is a very safe one, but entails much labour except on the smaller type of plant. The number of tests to be performed is very little less than with the previous method.

A great deal of this chemical work is obviated by the system of Dr. E. W. Smith. A certain amount of experimental work is first carried out in order to ascertain the temperatures, or cut points, which will give, on a standard laboratory apparatus, fractions corresponding to the pure products desired from the rectification still. When the latter is charged it is dipped and an average sample of the contents is taken. This is distilled in the laboratory and the number of gallons to be expected in each fraction worked out. These figures are given to the attendant, who controls the distillation merely by dipping his receiving tanks.

Edwards (*Proc. Eng. Junior Gas Assocns.*, 1916—1917) recommends the use of a boiling-point test in a special form of apparatus, and gives curves of boiling point and composition for various mixtures.

### Acid Recovery

The “acid tar” leaving the washer consists of a mass of resinous and tarry matter, together with an excess of sulphuric acid. The disposal of this material was formerly a source of considerable trouble. Now, however, the excess of acid is recovered by heating the “tar” with steam. The usual method consists in running the acid tar into shallow tanks and blowing steam through the mass. This has the effect of separating the material into two layers—one of dilute sulphuric acid, which may be run off and used in the sulphate plant; the other, a viscous pitch-like substance, which solidifies on cooling, and may then be tipped or burnt. A better method is to boil the mass by means of closed steam coils, constructed of chemical lead pipe; this yields a stronger acid, owing to the exclusion of condensed steam.

### Manufacture of Caustic Soda

Owing to the high price of commercial sodium hydroxide it is frequently cheaper to manufacture the caustic solution by the interaction of lime and soda ash—commercial sodium carbonate. The soda ash is added to water in a tank and the whole boiled up with steam, until a solution of about 1.1 specific gravity is obtained. Lumps of high-grade quicklime are placed in a tray made of wire mesh, and so supported that the lime is partly covered by the solution. The lime is disintegrated and washed away, fresh lumps being added to the tray until the quantity of lime used is equal in weight to the soda ash dissolved in the water. The result is a solution of caustic soda containing in suspension a precipitate of calcium carbonate. The latter is allowed to settle and the clear solution is then run off for use. The mud contains some caustic soda, and is therefore washed with water and again allowed to settle. The washings—dilute caustic solution—are used for dissolving the next batch of soda ash.

## CHAPTER XIV

### PRECAUTIONS AND DIFFICULTIES IN RECTIFYING

#### Fire

MENTION has already been made of the urgent necessity for taking every precaution against fire. This is important in the case of the debenzolising plant ; but even more so in the rectification of benzol, owing to the fact that large volumes of highly inflammable liquids are handled at temperatures approaching their boiling points. Not only should the distillation plant be amply protected, but the same applies to the benzol washer. The interaction of the sulphuric acid and the unsaturated constituents of the crude benzol generates a certain amount of heat. If the benzol contains much impurity the contents of the washer may become dangerously hot, and inflammable vapours will be evolved in consequence. The remedy in such a case is, of course, to stop the agitator and allow the liquids to separate by gravity and cool down, some washers being fitted with water-jackets to expedite this. In any case, however, a benzol washer should be housed in a separate building, well protected from any chance of ignition by gas engines, electric motors and switches, etc. At least one very serious disaster recently was traced to the starting switch of the electrically-driven agitator, when the latter was switched off on account of overheating of the benzol.

Otherwise the precautions to be taken and difficulties to be overcome in rectification are not serious.

#### Emulsification in the Washer

Failure of the aqueous layer to separate from the benzol often causes trouble and, in some cases, redistillation. The cause is emulsification, and the occurrence of this is sometimes most unexpected and difficult to explain. The trouble is most acute when washing the solvent naphtha fraction, and this constitutes another argument in favour of a primary distillation to one unwashed crude benzol. Emulsification sometimes occurs, however, in the washing of this material, and appears to be most serious in the case of the water-wash immediately following acid or caustic. For this reason the first water-wash after withdrawal of the acid tar should never be accompanied by agitation, but should be carried out by means of a length of hose, a gentle

spray of water being allowed to fall through the benzol and down the sides of the vessel. Subsequent water washings may be performed safely with the agitator at work. The same applies to the water-wash immediately after the use of caustic soda.

### Thick Acid Tar

If the acid tar is found to be very viscous and difficult of removal, this indicates an insufficiency of acid, or an excess of impurities. In washing once-run benzol this difficulty is very rarely encountered, since a large proportion of the unsaturated bodies is removed in the primary distillation. Conversely, of course, if the acid tar is very thin an excess of sulphuric acid has been employed.

### Water in Benzol

The presence of water in the benzol during washing dilutes the acid and in consequence renders it very much less effective. On this account a charge of benzol should be given ample time for settlement in the washer, and all traces of water should be drawn off before the introduction of the acid. The same applies to washed benzol, since the presence of water at the commencement of the final fractionation impairs the separating action of the process by causing steam-distillation effects before they are required.

### Paraffins

If pure products are desired, such as those required for the explosives or dyestuffs industries, the presence of paraffins is probably the greatest nuisance the rectifier has to face. The reasons for the presence of these bodies have been referred to, together with the impossibility of their removal by chemical means. The chief effect noticed with paraffinoid benzol is that the cut points are less distinct, and in consequence a larger volume of forerunnings and intermediates must be run. The reasons are two: firstly, the paraffin series contains members whose boiling points cover the whole of the crude benzol range; and secondly, many of these members form mixtures of constant boiling point with the benzene hydrocarbons. If paraffins are present in the crude, it is practically impossible to produce paraffin-free rectified products. The percentage of paraffins in the latter must be reduced as much as possible by a process of 'sweating-off,' *i.e.*, the distillation (particularly at the fore-running and intermediate stages) must be carried out very slowly, and very drastic dephlegmation must be applied. It should again be emphasised, however, that the presence of paraffins in motor benzol is of no moment—in fact, they may prove an advantage.

### Impure Products

A difficulty of a somewhat similar character is sometimes found in the inability to produce a sufficient yield of pure benzols. ("Purity" is here considered from the point of view of distilling range.) This, when it occurs, is nearly always due to some imperfection in the plant. Leaking steam coils form a possible cause, detected by the presence of water in the condensates before the admission of live steam. All coils and valves on the stills should on this account be periodically tested and overhauled. Otherwise the fault may lie in the fractionating column or in the dephlegmator. These must be efficient if good results are to be attained. The amount of liquid condensed in, and returned by, the dephlegmator should be from three to four times the volume of distillates leaving the condenser. The fractionating column must be protected from draughts, and a high and constant steam pressure (preferably at least 90 lbs. per square inch supplied through a reducing valve) is an essential.

### Evolution of Fumes

In certain instances the washing and subsequent refractionation of benzol has been accompanied by the evolution of fumes, usually sulphur dioxide. These are thought to be due to the decomposition of compounds formed during the acid washing, *e.g.*, normal alkyl sulphates. The occurrence of objectionable fumes is, however, so rare, and may be due to so many varying causes, that each case merits separate investigation. It is a very easy matter to conduct vent pipes from washers, separators, etc., outside the building.

### Naphthalene

Naphthalene blockages practically never occur on a rectifying plant, especially where a preliminary distillation into once-run benzol is effected, in which case the naphthalene remains in, and is subsequently cooled out from, the residue. The only likelihood of a blockage is in pipes conveying this residue, or the residue from the solvent naphtha stills. If the quantity of naphthalene in the crude benzol is excessive, such pipes should be fitted with steam connections and rodding holes.

### Solidification

It is almost superfluous to repeat that pure benzene solidifies at 5° C. Ignorance of, or failure to remember, this fact has at times led to some amusing "difficulties," for in frosty weather the contents of a pure benzol storage tank may be found to consist of masses of crystals.

### Corrosion

Owing to the preliminary washing, and also to the liberation of the gaseous impurities in the debenzolising plant, little corrosion need be feared in the rectification plant if due care is exercised with the water-wash. Any retention of caustic or acid in the washed benzol will, of course, lead to trouble, but two or three prolonged washes with water are usually sufficient to avoid this.

### Deposits

The question of efficient water washing is of more importance here. Deposits of sodium sulphate have been encountered on heating coils, and where the residues after washing are put back into the wash-oil similar deposits have been found in the heat exchangers and preheaters of the debenzolising plant. T. H. Butler has found a deposit of indefinite but highly carbonaceous composition on the heating coils when distilling paraffinoid benzols, whilst hard or "scaly" water often leads to trouble in dephlegmators and condensers. It must be remembered that such deposits act as heat insulators, and that frequent inspection and cleaning of these portions of the plant is advisable.

In conclusion, it must not be thought that the rectification of benzol is a difficult or intricate proceeding, or that all or many of the above difficulties will necessarily be encountered. Given an efficient type of plant and reasonable care the process is, in fact, a comparatively simple one, particularly when motor fuel is the objective. The latter is a process which the technical staff of any up-to-date gasworks could easily deal with.

## CHAPTER XV

### THE COST OF BENZOL RECTIFICATION

THE remarks made in Chapter IX. as to the difficulty of giving figures for the cost of any plant or process at the present time apply with equal force here. Nevertheless it is considered desirable to give some approximate figures which, modified at any time to the existing conditions, may form a basis for a balance sheet when the financial aspect of rectification is under consideration.

#### Cost of the Plant

Rectification plant, as has been seen, is in itself more complicated, and, therefore, more costly, than apparatus for debenzolising wash-oil. In the latter process, however, the bulk of material (wash-oil) to be handled on the basis of, say, 100 tons of coal is so much greater than the crude products obtained from that weight of coal that the plant required for rectifying crude benzol costs very little more than that required for its production.

The cost of the plant necessary for complete rectification of the crude benzol into pure products may be taken as from one to one and a half times the cost of the corresponding debenzolising plant, exclusive of steam boilers but including storage tanks, pumps, foundations, etc. This will amount to £8 to £16 per ton of coal carbonised per maximum day, the smaller plants being, of course, relatively the more expensive.

The production of motor spirit entails a much simpler plant, and in this case the capital outlay will be from £3 to £8 per ton of coal, these costs being given, as before, on a pre-war basis. The cost of very small units does not in this case rise in as great a degree, since the agitation is frequently performed by hand and the cost of a mechanical agitator thereby avoided.

#### Labour

Labour charges in rectification are a comparatively small item. In the average gasworks the process may be carried on in the daytime only, and one man can comfortably attend to a plant yielding 700 gallons of pure products per day. With smaller outputs the operation of the rectifying plant occupies only a portion of one man's time, and the attendant should have other duties—near at hand—assigned to him. These may



usefully include the supervision of the debenzolising and tar-dehydrating plants, together with the firing of a boiler if a separate one be installed for these purposes. These remarks apply in a greater degree to the less intricate process of motor benzol production.

In any case, skilled technical supervision is also necessary.

### Cost of Materials

The quantities of sulphuric acid used vary with the character of the crude spirits. Taking acid at £5 per ton, an average cost for acid washing would be 8s. per ton of rectified products.

If crude benzol from oil washing only is washed, the consumption of caustic soda will be very small, say, from 1s. to 1s. 9d. per ton of products, since the soda is only required to remove the traces of acid remaining after washing with water. If crude naphtha from coal-tar be washed, an additional, and more drastic, washing with caustic is effected before the acid wash in order to remove tar-acids.

### Steam Consumption

As so much oil is returned by the fractionating column and dephlegmator, it may be thought that benzol rectification necessitates the provision of a large weight of steam. It must again be remembered, however, that the total volume of benzol rectified represents a very small proportion of the benzolised oil which was heated by means of steam for its production. In fact, the consumption of steam on a rectification plant—which is invariably steam-heated—is somewhat less than that of the corresponding debenzolising installation. Fifteen shillings to 18s. per ton of products will in most cases cover expenses under this head.

### Water

A supply of cold water is required for the condenser and dephlegmator, and owing to the action of the latter the quantity exceeds that necessary for condensation on the debenzolising plant. An average figure is 3—4 gallons of water per gallon of distillate. The much larger water consumption of the oil coolers is not required here.

### Total Cost

It is hoped that the foregoing data will serve as a guide to those contemplating the installation of rectification plant. It will in most cases be found that the total cost of rectifying benzol amounts to between 2d. and 3½d. per gallon of products, the lower figure applying to the manufacture of motor benzol. Interest on capital outlay, depreciation, and maintenance may be taken together at 17 per cent. per annum.

# PART III

## THE USES OF BENZOL AND ITS PRODUCTS

### CHAPTER XVI

#### ARTIFICIAL DYESTUFFS, DRUGS, ETC.

IN considering the commercial utilisation of benzol and its products, it is perhaps natural that the so-called coal-tar dyes should at once occur to the mind. The study of artificial dyestuffs forms in itself a vast and absorbing subject, and the record of progress made by the synthetic chemical industry in all its branches is one which reflects the greatest credit on both chemists and engineers responsible for it, and for the enormous amount of research work which of necessity preceded and still forms an essential part of the various processes.

In addition to the large number of synthetic drugs, perfumes and chemicals now available, there are on the market upwards of a thousand distinct artificial dyestuffs, which, moreover, are dealt with under some four or five thousand trade names. In view of this, and of the extreme complexity of these substances and the processes involved in their manufacture, it is obviously impossible to give even an outline of the industry in such a book as this. On the other hand, it is felt that no book on the subject of benzol would be complete without some reference to this important outlet for that spirit, and it is hoped that the following brief survey will prove of some interest.

#### The Artificial Dyestuffs Industry

The coal-tar colours were formerly classed under the heading of "Aniline Dyes," and this name was correctly applied in the first instance, for the earlier dyestuffs were derived from aniline. This substance was first obtained from natural indigo (Portuguese, *Anil*) by Unverdorben in 1826, and eight years later Runge isolated it from coal-tar. It was whilst using aniline in an unsuccessful attempt to synthesise quinine that W. Perkin discovered the first synthetic dyestuff, Mauve or Aniline Purple,

in 1856. This colour was successfully manufactured and others were developed from this accidental discovery, but it may be truly said that the subsequent enormous development in the manufacture of synthetic organic products was based upon the hypothesis of Kekulé regarding the structure of the benzene molecule. This theory, to which we have previously referred (p. 1), was advanced in 1865, and its application has made it possible to build up a multitude of complex substances, and even, in some cases, to foretell their existence and properties before the substances themselves have been isolated.

Practically all the artificial dyestuffs now on the market require for their preparation some constituent of coal-tar, and, with the exception of anthracene from which the important alizarin dyes are produced, all these constituents are present in crude benzol. Large quantities of benzene, toluene, xylene and naphthalene are used in the various processes, and phenol and aniline are also of the utmost importance. The last two compounds do not exist as such to any appreciable extent in crude benzol. The amounts present in tar are also relatively small, and in fact the extraction of aniline from tar is commercially impossible. As a result large quantities of both these substances are now prepared synthetically from benzene, and should, therefore, be classed more logically as "intermediates."

But whilst the aromatic compounds are essential as a starting point for these various manufactures, it must not be thought that they constitute the only important requirements. These compounds form, in fact, only a relatively small component of the finished product, and abundant supplies of other chemicals—notably sulphuric acid, both "concentrated" and "fuming," nitric acid, chlorine, ice, etc.—are quite as essential as are the coal-tar derivatives.

The reasons for the transfer of the bulk of the dye industry from this country to Germany have been discussed on many occasions and from many points of view. It has often been overlooked, however, that in the years immediately preceding the war, although we were importing from Germany dyes to the value of some £2,000,000 annually, we were at the same time actually supplying the German manufacturers with large quantities of intermediate products necessary for the production of those dyes.

During the past five years much progress has been made in the manufacture of synthetic products in this country, and the least tribute we can pay to our dyeworks chemists and engineers is to remember that, faced not only with an unprecedented demand, but also with acute shortage of plant, labour and materials, and with the diversion of the bulk of the benzol, toluol and acids to the manufacture of explosives, they yet succeeded in producing sufficient dyestuffs for the uniform and equipment of both our own forces, and those of many of our Allies. This fact

alone augurs well for the future, and although the demands for motor-benzol will probably be much greater, the benzol consumption of the synthetic chemical industries will be a considerable and increasing one, the fostering of which will materially assist the commercial prosperity and military safety of the nation.

### Intermediate Products

Before the desired product is obtained the aromatic hydrocarbon which forms the nucleus must pass through a number of intermediate stages, entailing reactions of great complexity in some instances. In fact, the preparation of the intermediate products very frequently becomes more difficult than the production of the dyestuff or drug from those intermediates. It has been stated with regard to the dye industry that there are nearly one hundred intermediates of importance, each one of which entails from six to twenty separate chemical operations in its preparation. When it is considered that each of these operations necessitates the use of expensive plant, acids and other chemicals, the relatively high cost of dyestuffs will be understood. Some typical intermediates may now be mentioned.

#### *Nitrobenzene*

Nitrobenzene,  $C_6H_5NO_2$ , is probably the most important derivative of benzene. It is prepared by stirring benzene with a mixture of concentrated nitric and sulphuric acids in water-cooled cast-iron vessels (*see* FIG. 63, p. 180). It is important that the temperature be kept below  $25^\circ C.$ , as otherwise the formation of dinitrobenzene would occur. The reaction for the nitration is expressed by:—



the sulphuric acid being introduced solely to absorb the liberated water. Nitrobenzene is a heavy yellow liquid, boiling at  $205^\circ C.$ , and possessing a distinctive odour. It is known as Oil of Mirbane.

#### *Aniline*

Aniline, aminobenzene,  $C_6H_5 \cdot NH_2$ , is an important compound from which mauve, magenta and various blue and black dyes are produced. It is prepared by the acid reduction of nitrobenzene, and this is effected in practice by heating the nitrocompound with hydrochloric acid and iron borings. Nascent hydrogen brings about the reduction, and the aniline, which is a colourless oil boiling at  $184^\circ C.$ , is distilled from the mixture.

The apparatus in which such a reduction is carried out is shown diagrammatically in FIG. 62. It comprises a cast-iron cylinder, usually of 500 or 600 gallons capacity, and containing a vertical hollow shaft and paddle agitator. The cylinder is charged with

the requisite quantities of nitrobenzene and hydrochloric acid, and the mixture heated by steam blown through the hollow shaft. Part of the steam enters at B, A being a supply of steam derived from "aniline water"—the water separated from a previous distillation. The steam is now shut off and a quantity of clean iron borings is gradually added through the feed-hopper

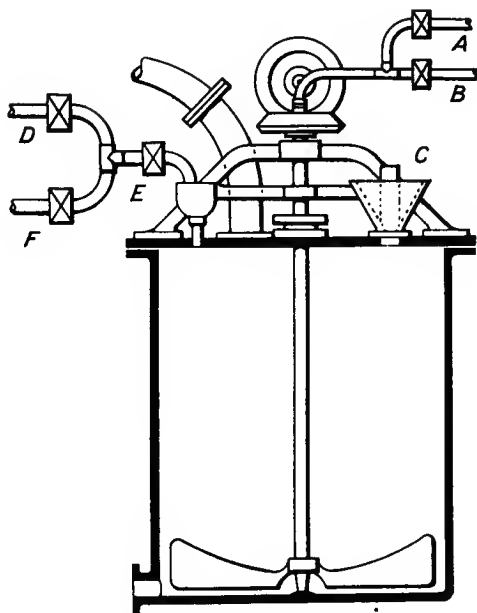


FIG. 62.—ANILINE APPARATUS.

C. The reaction is exothermic, and a mixture of aniline, nitrobenzene and water distils off and is returned by the pipe D to the cylinder. When the reaction is complete steam is again introduced and cock E is closed, the distillate of aniline and water passing away through F.

#### *Aniline Derivatives*

*Diphenylamine* and *Para-nitraniline* are two of the important intermediates prepared from aniline, and therefore, indirectly, from benzene.

The alkaline reduction of nitrobenzene gives *Azobenzene*, from which the important substance *Benzidine*,  $\text{NH}_2 \cdot \text{C}_6\text{H}_4 \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2$ , is prepared, the nascent hydrogen in this case being obtained from zinc dust and caustic soda.

*Benzene-sulphonic Acid*

Benzene-sulphonic acid,  $\text{C}_6\text{H}_5 \cdot \text{SO}_3 \cdot \text{H}$ , is prepared by the interaction of benzene and fuming sulphuric acid under suitable conditions. It is of great value as an intermediate.

*Phenol*

Phenol,  $\text{C}_6\text{H}_5 \cdot \text{OH}$  (known as carbolic acid), has been referred to as an intermediate, since large quantities of great purity have been obtained synthetically from benzene. Benzene-sulphonic acid is treated with milk of lime, giving the calcium salt. Further treatment with sodium carbonate gives sodium benzene-sulphonate which is evaporated to dryness and fused with caustic soda. The product is sodium phenolate, from which phenol is readily obtained by the action of dilute acids. Theoretically 1 ton of benzene should give 1.2 tons of phenol, but in practice only some 70 per cent. of this yield is obtained.

*Chloro-benzene*

Chloro-benzene,  $\text{C}_6\text{H}_5 \cdot \text{Cl}$ , is also much used in dye manufacture.

*Corresponding Substances*

These compounds have been cited as examples of what may be termed the "primary intermediates," and corresponding bodies are derived from the other aromatics. Thus nitro-toluenes and toluene-sulphonic acids are prepared respectively by the nitration and sulphonation of toluene; nitro-naphthalenes and naphthalene-sulphonic acids from naphthalene, and so on.

*The Naphthols*

The naphthols,  $\text{C}_{10}\text{H}_7 \cdot \text{OH}$ , form the starting point in the manufacture of many colours, and are obtained from the sodium salts of the naphthalene-sulphonic acids.

The above examples all relate to fairly simple and well-known compounds, and the list might be prolonged almost indefinitely. As a type of a more complex intermediate we may finally consider the valuable "*H acid*." This is an amido-naphthol-disulphonic acid. It is prepared, through many stages, from naphthalene and forms the basis of a large number of important dyes.

**Coal-Tar Dyes**

Artificial dyestuffs are classified by the manufacturer according to their chemical composition, whilst the user further subdivides them with reference to the method of their application or to their action on the material to be dyed. Thus, if pieces of wool and

cotton be dipped into a solution of picric acid they will absorb the dye and will be yellow when withdrawn. It will be found, however, that while the yellow colour can be washed out of the cotton with water, it cannot be so removed from the wool, in which the dye is fixed. On the other hand, if cotton be immersed in a solution of chrysophenine it will be dyed a permanent yellow. Chrysophenine is therefore classed as a Direct Cotton Dye. Similarly, Mordant Dyes are those which require some other reagent—usually a metallic salt—to fix them upon the fibre, by the production therein of an insoluble colouring matter; different colours may sometimes be produced with the same dye by the use of various mordants. Vat dyes again are insoluble colouring matters which are dissolved in the vat by reduction. The material to be dyed is treated with the solution, and the colour is subsequently developed in the fibre by oxidation, usually exposure to air. Artificial indigo is an example of this class of colours. In the case of Sulphide Dyes the reduction is effected by a sodium sulphide bath.

As regards chemical composition the chief group is that of the *Azo Dyes*; these include a very large proportion of the dyestuffs of commerce, and each contains a group consisting of two nitrogen atoms, thus:—



The azo dyes are, therefore, very numerous, and vary considerably in composition and mode of application. Thus Aniline Yellow (para-amidoazobenzene) and Crystal Scarlet (a product of naphthol-disulphonic acid) are respectively basic and acid azo colours, whilst Hessian Purple N is a disazo direct cotton dye.

Benzene, toluene, xylene and naphthalene all give rise to numbers of colouring matters falling within the above and other groups, but the chief vat dyes are obtained from naphthalene and anthracene, the former being the usual starting point in the production of indigo and the indigoid vat colours.

### Indigo

Indigo is probably the most important of all the synthetic colouring matters, enormous quantities being used annually. Until comparatively recent years the indigo requirements of practically the whole world were met by the natural product emanating from the Indian plantations, which, in consequence, largely controlled the markets. Synthetic indigo was prepared by Baeyer in 1880, starting from toluene. This raw material was scarce and costly, and it was not until 1897 that the artificial dye was able to compete with the Indian product. The remarkable development of the manufacture since that date is well known. The Indian exports of natural indigo in 1896 were valued at over £3,500,000, and the price of the dye was about 8s. per lb., but in the year 1913 these figures had fallen to £60,000, and

3s. 6d. respectively. And it should here be noted that, although termed "artificial," the quality of synthetic indigo is equal, if not superior, to that of the natural product.

Two processes are available for the manufacture of indigo, both very complicated and both necessitating the use of large quantities of fuming sulphuric acid, glacial acetic acid, and chlorine.

In the first process naphthalene is the raw material, and is heated with sulphuric acid and mercury (as a catalyst) to produce phthalic acid. Ammonia converts this into phthalimide which is chlorinated to anthranilic acid, further steps leading to phenylglycine-*o*-carboxylic acid, indoxyl, and finally indigo.

The second process begins with aniline and may therefore be said to use benzene as the starting point. Aniline is heated with chloracetic acid, by which means phenylglycine is obtained and subsequently converted into indoxyl and thence to indigo.

### Synthetic Drugs, etc.

Progress in the manufacture of drugs, antiseptics and other products during recent years has been, if possible, more remarkable than the development of the dyestuffs industry. It is only possible to mention here a few typical synthetic products, and to indicate their relation to the constituents of benzol.

#### *Antifebrin*

Antifebrin, acetanilide, is one of the oldest synthetic drugs and is of great use as an antipyretic. It is prepared by the interaction of aniline and glacial acetic acid.

#### *Phenacetin*

Phenacetin, derived from phenol, is much less toxic than antifebrin whilst being as effective as a febrifuge. It has thus largely replaced the latter drug.

#### *Antipyrin*

Antipyrin is much used for the same purpose and is prepared from phenylhydrazine, a derivative of aniline.

#### *Salicylic Acid*

Salicylic acid, largely used in medicine and as a food preservative, is likewise derived from phenol; and one of its preparations is the well-known anti-rheumatic Aspirin, acetylsalicylic acid.

#### *Other Drugs derived from the Benzene Series*

The valuable local anæsthetics, *Eucaine* and *Novocaine*, are derivatives of the benzene series, whilst *Salvarsan* is a highly



complex compound of benzene and arsenic. *Flavin* and *Trypaflavin* are dyestuffs which have recently been found to possess valuable antiseptic and bactericidal properties. Phenol, which is probably the oldest antiseptic, is being rapidly replaced in modern surgery by the various synthetic products now available.

### *Saccharin*

Saccharin, or benzoic sulphimide, is obtained from toluene through the medium of toluene-sulphonic acid. Saccharin is five hundred times as sweet as cane sugar, but is almost insoluble in water, the common form being the easily soluble sodium salt.

Sufficient has been said to indicate the close relation between the production of crude benzol and the manufacture of synthetic chemicals, which embraces a multitude of substances in the foregoing, and many other, categories. Many perfumes and flavouring matters are now widely used which owe their popularity to the fact that they can be synthesised from benzol products at a cost far below that of the corresponding natural substance; and in conclusion we may note that photography is to-day dependent on benzene derivatives. Not only are most of the developers prepared synthetically from that source, but coal-tar dyes enter very largely into the manufacture of the various panchromatic and orthochromatic plates, light filters, and the like.

## CHAPTER XVII

### EXPLOSIVES

AN explosive is defined as a material which is capable of suddenly emitting a very large volume of gas. A great variety of explosives is available, and although there is a tendency to associate their use with warfare only, it must be remembered that explosives are used in a large number of peace-time industries. Military explosives are divided roughly into propellants and high explosives, the former being, in general, slow-burning mixtures when their velocity of decomposition is compared with that of the more violent class. Propellants, which are not commonly derived from benzol products, will not be further discussed.

#### Aromatic Nitro-explosives

Most modern high explosives are nitro-derivatives of the aromatic hydrocarbons, chiefly of benzene, toluene and naphthalene, and it was on this account that the recovery of crude benzol became a matter of vital importance during the war. It will be seen that the manufacture of these explosives is very closely related to the synthetic dyestuff industry, and, in fact, not only is lyddite, or picric acid, a dyestuff in itself, but the production of the other nitro-explosives necessitates the use of many of the intermediates which form stages of such importance in the manufacture of colouring matters. This will be clearly indicated in discussing a few typical explosives which owe their origin to the constituents of crude benzol.

#### High Explosives

The modern high explosive, whether for military or civil use, is a nitro-derivative of an aromatic hydrocarbon, the commonest being picric acid, trinitrotoluene and mixtures of the latter nitrate with various other substances. Nitro-compounds of naphthalene and of aniline are also extensively used.

In addition to being unstable, and, therefore, more or less easily detonated, these nitro-compounds are very effective as high explosives; for not only does their combustion liberate large volumes of nitrogen, but they also contain in the acid radicle a large proportion of the oxygen necessary for complete combustion. In general the most powerful explosive is one

which gives rise to the greatest volume of gases and at the same time requires little external oxygen. In this connection *Table 27* is of interest, tetranitraniline being the most effective of the modern high explosives.

TABLE 27.—NITROGEN CONTENT AND OXYGEN REQUIREMENTS OF EXPLOSIVES (*Colver*).

EXPLOSIVE.	Percentage N <sub>2</sub> .	Grammes O <sub>2</sub> required for combustion of 100 grammes.
Dinitrotoluene. .	15.4	114
Trinitrotoluene .	18.5	74
Picric acid .	18.3	45
Tetryl . . .	24.4	47
Tetranitraniline .	25.6	32

The most important properties of an explosive are its power, violence, and relative insensitiveness. Power is measured by the volume of gas liberated per unit weight of explosive and is therefore an indication of the amount of work the explosive will perform. Violence is in reality the velocity of propagation of the explosion through the material. Thus a high explosive is required to have a high velocity, whilst for a propellant a less violent and slower burning preparation is used. Insensitiveness to shock is a relative term and is measured by the height from which a known weight must be dropped before detonating the explosive. The last is obviously a most important property in the handling, charging and use of the material. *Table 28* gives figures which indicate approximately the characteristics of common high explosives.

TABLE 28.—PROPERTIES OF HIGH EXPLOSIVES.

EXPLOSIVE.	Velocity of detonation. Metres per second.	Relative power.	Relative insensitiveness.
Trinitrotoluene .	7,000	95	115
Picric acid .	7,300—7,500	100	100
40/60 Amatol .	6,400	116	—
80/20 Amatol .	4,800	127	120
Tetryl . . .	7,200	120	70

### Explosives derived from Benzol Products

In the preparation of all the modern high explosives the process of nitration plays the principal part. In some cases the

hydrocarbon is first sulphonated, whilst in others nitration is direct. The nitration itself is comparatively simple, and reference has been made to it in the foregoing chapter. The question of temperature control, however, must be closely studied, for the reactions are vigorous, and not only does the temperature of formation affect the structure of the nitro-molecule, but many stages of the operation are attended by grave risks if the temperature be allowed to rise. For this reason water-cooling devices must be incorporated in the plant used. These may take the form of a water jacket or, better, of coils of lead pipe immersed

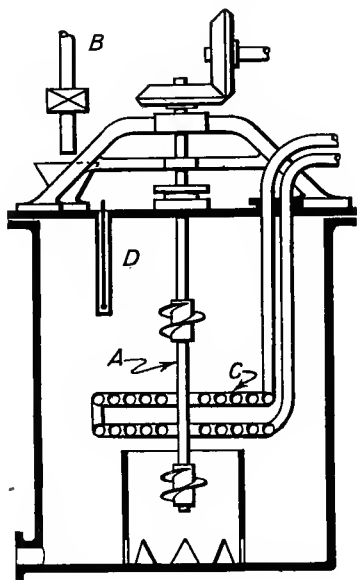


FIG. 63.—APPARATUS FOR NITRATING BENZENE.

in the liquids, and through which water is passed. The latter form of apparatus is shown diagrammatically in FIG. 63, which illustrates a benzene nitrator. This consists of a cast-iron tank of some 1,000 or 1,500 gallons capacity, provided with a high-speed agitator A, driven by bevel gearing, and with acid inlet at B. Coils of lead pipe C, through which water is passed, serve to control the temperature of the reaction indicated by a thermometer in pocket D.

#### *Picric Acid*

Picric acid (trinitrophenol) was, under the names Lyddite or Melinite, the first of the aromatic nitro-explosives to be used, and is a derivative of benzene by way of synthetic phenol. Phenol

is first sulphonated by dissolving it in an excess of concentrated sulphuric acid, and the phenol-sulphonic acid is then treated gradually with the requisite quantity of nitric acid. Large quantities of nitrous fumes are evolved and there remain in the pot solid picric acid and dilute sulphuric acid. The former is washed, ground and dried. The efficiency of the process is commonly about 57 per cent., the theoretical yield being nearly 3 tons of picric acid per ton of phenol, and the practical about 1·7 tons.

Picric acid is a very powerful and violent explosive, but is somewhat sensitive to percussion. Its chief disadvantage, however, is its liability to form highly sensitive picrates of metals such as iron or lead with which it may come into contact. Its use is always attended with danger from this fact, though special precautions, such as enamelling the interior of the shell, have been taken. Large quantities of picric acid were used during the war, especially by the French and Italians, and it formed practically the sole high explosive in the South African campaign and the Russo-Japanese war. In modern warfare it has been largely displaced by the safer T.N.T.

#### *Trinitrotoluene.*

Trinitrotoluene (T.N.T. or trotyl) is prepared by the direct nitration of toluene, usually in three stages. A mixture of nitric and sulphuric acids is used—the latter to absorb the liberated water—and the toluene is first converted into mononitrotoluene with waste acids from subsequent nitrations. During the second treatment with acid, the contents of the vat are kept at about 90° C. by means of steam, and finally cooled. Solid dinitrotoluene separates out, and a third nitration with fresh acid produces T.N.T.—also a solid. This is washed with cold water, broken up, washed with potash and water, and dissolved in a mixture of alcohol and benzene with the aid of steam. On cooling the solution, pure T.N.T. crystallises out, and is centrifuged and finally sieved. One ton of toluene gives in practice about 2 tons of T.N.T., the efficiency of conversion being about 70 per cent.

Although trinitrotoluene is less powerful and somewhat less violent than picric acid (*Table 28*, p. 179), it is also less sensitive and therefore safer in use and transport. T.N.T., however, offers the great advantage that it has no tendency to form sensitive compounds with metals, and the risk of premature explosion is practically eliminated. It also melts at a lower temperature than lyddite, and the danger of filling the shell is correspondingly reduced. As a result of these advantages T.N.T. was the principal high explosive of the early part of the war. It was, however, comparatively costly, and it was soon found that the supply of toluene was unequal to the demand. It had also been found that the detonation of trotyl gave rise to large volumes of black

smoke—in other words, combustion was incomplete, and the whole of the available power was not realised. Whilst, therefore, some workers were attempting to produce synthetic toluene on a commercial scale, others were experimenting with certain composite explosives, in which an oxygen carrier was mixed with, and assisted the combustion of, the high explosive.

#### *Amatol.*

Amatol, a mixture of trinitrotoluene and ammonium nitrate, became by far the most generally used shell-filling of the war. Several mixtures were used and were designated by the figures representing their percentage composition. Thus 80/20 amatol contained 80 per cent. of ammonium nitrate and 20 per cent. of T.N.T. This mixture, and also 40/60 amatol, were very widely used, for they offered many advantages. In the first place the adoption of amatol greatly increased the number of rounds which could be filled with a given weight of T.N.T. Again it will be seen from *Table 28* (p. 179), that amatol is at once less sensitive and much more powerful than the undiluted trotyl. Large quantities of ammonium nitrate were available, and the cost of amatol was only about one-third of that of T.N.T., whilst the mixture was also, of course, less poisonous. The only objection to the use of amatol was its lower velocity of detonation, although even this fact proved in some cases an advantage.

#### *Tetranitraniline.*

Tetranitraniline, obtained by the action of potassium nitrate and sulphuric acid upon mononitraniline, is an exceedingly powerful explosive. It possesses the highest nitrogen content and contains the greatest proportion of the required oxygen, of all modern high explosives. It is remarkably stable, has no dangerous action on metals, and can be manufactured in bulk, since the reaction is easily controlled. It offers many advantages and has been widely used in detonators, but is rather too sensitive for a shell filling.

#### *Tetryl.*

Tetryl (tetranitromethylaniline) is only slightly less powerful than tetranitraniline. It is of about the same sensitivity as lyddite, but is very poisonous. It is prepared by the nitration of dimethylaniline, and is a very violent explosive. On this account it has found wide application in the charging of detonators and mines.

Many other mixtures and compounds are used as high explosives in modern warfare, and the great majority are derived from benzol products. The *nitrobenzenes* are useful in this connection and in the preparation of commercial explosives, and others are

*trinitrocresol* (similar to picric acid) and *trinitroanisol*. Amatol to which has been added charcoal and aluminium powder gives *ammonal*, a filling for hand grenades.

### Commercial Explosives

Although warfare naturally gives an enormous stimulus to the manufacture of explosives, they have very many industrial applications, among which may be mentioned blasting, coal-mining, breaking up subsoil, removing tree trunks and ice-breaking, as well as general demolition work. Most of the above-mentioned explosives would be suitable for these purposes, but there are legal restrictions on their use, and the list of " Permitted Explosives " contains in general those of very low sensitivity. It is only possible to notice a few examples here.

#### *Ammonite and Roburite.*

Ammonite contains 88 parts of ammonium nitrate and 12 parts of dinitronaphthalene.

Roburite also contains 88 per cent. of ammonium nitrate, the remainder being 11 of dinitrobenzene and 1 of chloronaphthalene. The explosives now permitted are often diluted with some inactive substance. Thus *Negro Powder No. 2* contains 57 per cent. ammonium nitrate, 15 per cent. T.N.T., 27.5 per cent. of sodium chloride, and 0.5 per cent. of graphite.

### Chlorate and Perchlorate Mixtures

These mixtures are not extensively used for military purposes, but are sometimes preferred for engineering work, particularly in coal mines. Unless special precautions are taken—as in *cheddite*, where the oxygen carrier is coated with vegetable oil—chlorate explosives are dangerously sensitive. Perchlorate mixtures, however, are far safer in this respect and also contain more oxygen; they are therefore more widely used than the former.

### Safety Explosives

Many of the permitted explosives would be a source of danger if detonated in a coal-mine in which " firedamp " (methane) was present. In such a case a special safety mixture is used containing, besides the high explosive and sodium chloride, a considerable proportion of ammonium oxalate which reduces the temperature and length of flame.

## CHAPTER XVIII

### BENZOL AS A MOTOR FUEL

NOTE. *Throughout this chapter the word "benzol" relates, except where otherwise stated, to a grade of rectified benzol suitable for use in motors, such as, for example, benzol conforming to the motor fuel specification of the National Benzole Association.*

#### Possibilities of Motor Benzol

The quantity of benzol and its products annually required by the manufacturers of dyestuffs, drugs, and other synthetic chemicals, and of explosives, is likely to be very large and to increase, although remaining far short of the requirements of war time. But it is in the motor spirit market that benzol producers will find by far the largest outlet for their product. The demand for motor fuel is rapidly increasing from year to year, but the chances of finding a natural source of petrol in this country appear to be remote, and not only are the world's petroleum fields becoming gradually exhausted, but we also have, in the opinion of eminent geologists, to look forward to the time when naturally occurring motor spirit will be either non-existent or, at best, so expensive in production as to prohibit its practical use. The imperative need of rendering this country independent of other nations in regard to munitions of war (and motor spirit is essential in this respect) is too fresh in the memory to be overlooked. In fact, the conservation of every description of fuel is a subject of paramount importance at the present time. It is exceedingly unwise, if not criminal, to consume any fuel inefficiently, or less efficiently than it can be utilised in some other process. This consideration alone should be sufficient to extend the practice of oil washing to the whole of the gas industry, Coke-oven plants are to-day almost entirely equipped in this respect, and it is, therefore, to gasworks that we must look for an increase in the national output of liquid fuel. On a commercial basis, too, and having regard to the selling of gas in terms of heat energy, the benzol contained therein is worth only one-third or one-quarter of the value it possesses when extracted and marketed as a liquid.



### Suitability of Benzol for Use in Motors

It has been proved beyond the slightest doubt that benzol is an excellent fuel for the internal combustion motor, and the benzol producer no less than the motorist owes a debt of gratitude to the Automobile Association and Motor Union for its work on this subject. As long ago as 1907, this body appointed a committee to investigate the motor fuels then available, and subsequently published a report containing the committee's findings and recommendations. One of these was :

"That the attention of members of the Motor Union be directed to the use of benzol, either alone or in combination with petrol, as a motor fuel, since it can be used with complete success with the present types of engines and carburettors. Moreover, it is a home production, and more economical in use than petrol at the present time."

Owing to the steadily increasing demand for motor fuel, coupled with a much smaller increase in its output, the petrol of those days was a vastly superior fuel to that at present obtainable, which is a much heavier spirit owing to the inclusion in it of a larger proportion of the higher boiling fractions of the crude petroleum. On the other hand, cars and engines have greatly improved in design since that date. Many of these improvements, and particularly the almost universal substitution of the spray carburettor for that of the evaporative type, facilitate the use of a much more varying class of fuel in the same engine, with little or no adjustment. In fact, it may be truly said that any modern and efficient petrol engine can be made to consume benzol quite as efficiently, the alteration being made practically without trouble or expense. This expresses the result of some years' practical experience, for prior to the war large quantities of coke-oven benzol were used for motor spirit. The theoretical or scientific aspect of the subject is equally obvious, as has been proved by numerous contributors to the *Transactions of the Institution of Automobile Engineers*, and other workers.

According to Sir Dugald Clerk, the requirements of a suitable motor fuel are as follows :—

- (i.) Easy starting from cold.
- (ii.) Absence of objectionable odour, both in the fuel itself and in the exhaust products.
- (iii.) No liability to form deposits in the cylinders and valve passages.
- (iv.) Economical consumption.

To these may be added :—

- (ii. a.) No liability to cause excessive corrosion in any part of the engine.
- (iii. a.) No adverse effect on the lubricating oil or system of lubrication.

**A.A. and M.U. Tests, 1919**

The Automobile Association has recently arranged very thorough practical tests which prove beyond doubt that benzol completely satisfies all these requirements, and that it is both satisfactory and economical as a motor fuel. These tests were carried out under actual running conditions in autumn weather on all kinds of roads. Independent observers were present throughout and conditions were carefully noted, the fuel used during the whole of the tests being benzol conforming to the specification of the National Benzole Association (p. 135).

The first test consisted of a run of no less than 10,000 miles on a new 16-h.p. water-cooled "Sunbeam" car. The average weight of the loaded car was 1·8 tons, and the results of the test as to fuel and oil consumption were as follows:—

Average miles per gallon of benzol . . .	24·57
Average ton-miles per gallon of benzol . . .	44·22
Average miles per gallon of lubricating oil . . .	1,739·13

The second test was carried out under similar conditions, but the motor used was a 4 h.p. air-cooled "Triumph" motor-cycle and sidecar, the distance run being 5,000 miles. The corresponding results of the second test were:—

Average miles per gallon of benzol . . .	84
Average ton-miles per gallon of benzol . . .	31·34
Average miles per gallon of lubricating oil . . .	1,166

**R.A.C. Tests, 1920**

Similar tests were afterwards carried out by the Royal Automobile Club with equally satisfactory results. The first was a run of 10,000 miles on a 40/50 H.P. Rolls-Royce Car, the fuel being supplied by the National Benzole Association. The results were as follows:—

Average miles per gallon of benzol . . .	17·82
Average ton-miles per gallon of benzol . . .	42·87
Average miles per gallon of lubricating oil . . .	935·25

The second R.A.C. trial was carried out on a "G.N." two-seater car during a run from London to Edinburgh—approximately 400 miles. "National" benzol was again used and gave the following performance:—

Average miles per gallon of benzol . . .	59·8
Average ton-miles per gallon of benzol . . .	42·6
Average miles per gallon of lubricating oil . . .	316·4

These results compare very favourably with any obtainable on petrol, and the condition of the engine as regards wear, corrosion and lubrication was satisfactory in each case. These points will be mentioned in turn—it is proposed to deal now with the above-mentioned requirements of a motor fuel as applied to benzol.

### Easy Starting from Cold

The ease of starting depends primarily on the volatility and vapour pressure of the fuel, and it may be at once admitted that benzol is far less volatile than the petrol of five or six years ago. Owing, however, to the increase in specific gravity—and corresponding decrease in vapour pressure—of petrol, the difference in this respect between the two fuels has become practically negligible; and if an engine will start up easily on present-day petrol it may safely be expected to do so on benzol. Moreover, a return to the old grade of petrol cannot be anticipated, and a still further increase in specific gravity is probable from year to year. Immediately the engine becomes warm this starting difficulty of course disappears.

Pure benzene solidifies at about  $6^{\circ}\text{C}$ ., but the freezing points of toluene, xylene, etc., are progressively much lower. Motor-benzol of a suitable grade, such as that of the N.B.A., contains sufficient toluene and other compounds to prevent any solidification in the tank at temperatures reached in this country. The freezing point of National benzol has been given as  $7^{\circ}\text{F}$ . (25 degrees of frost). The admixture of a small proportion of petrol still further reduces this point. This addition of petrol may also prove advantageous where undue difficulty is experienced in starting, since peculiarities of the engine and other factors enter into the question, besides the vapour pressure of the fuel.

### Odour of the Fuel and of the Exhaust Products

The odour of properly rectified benzol is certainly no more unpleasant than that of petrol. The prevention of an offensive exhaust depends mainly upon:

- (a) Completeness of the combustion,
- (b) Sulphur content of the fuel.

The combustion of the fuel in the cylinder must necessarily be complete if efficient running is to be assured, and depends in turn upon the questions of carburation and mixture strength. Most modern carburettors will serve for benzol without alteration, particularly if an extra air supply is fitted. In practice benzol requires rather more air than petrol, and this is usually best arranged for by reducing the size of the jet by some 10 or 12 per cent. (It should be noted that this does not reduce the power of the engine, owing to the higher calorific value of the home-produced fuel.) The theoretical mixture for complete combustion of benzene is roughly 1 of benzene to 38 of air by volume, and this represents about 13 lbs. of air per lb. of benzene, against 14 lbs. of air required by each 1 lb. of petrol. Motor benzol, however, contains higher boiling aromatics, and the presence of these together with the greater carbon:hydrogen ratio of the spirit account for the larger proportion of air required in practice.

The specific gravity of benzol is some 20 per cent. higher than that of petrol, and this produces greater buoyancy of the float in the carburettor. Should this interfere with the supply of fuel to the engine the weight of the float can very easily be increased to the extent of 20 per cent. by the addition of a small lead washer of the required weight.

It may here be mentioned that some American cars—usually of the older types—are fitted with carburettors containing cork floats coated with varnish. This varnish is frequently soluble in benzol. In such a case the varnish should be removed by washing in benzol, the cork thoroughly dried and re-coated with a celluloid varnish, made by dissolving celluloid in acetone.

### Corrosion of Engine Parts

The question of corrosion of the engine parts also primarily depends upon the sulphur content of the fuel, and this will be discussed later. It may be at once noted, however, that in the 10,000-mile and 5,000-mile tests quoted above the engines were subjected to detailed and expert examination before and after the run. In neither case was it possible to observe undue overheating, wear or corrosion as compared with similar performances on petrol.

### Sulphur Content Permissible

A Committee of the Royal Automobile Club has reported that :

Anything up to 250 or even 300 grains of sulphur per gallon of spirit may be allowed, without a malodorous exhaust being produced, or any chemical action being caused on the metals in the engine.

On the other hand, Edmond Ledoux, giving evidence before the Motor Union Committee of 1907, stated that he had used *unwashed* 65's benzol in a 16-h.p. car with every success, and that "the odour of the fuel itself was worse than that of the exhaust." The National Benzole Association specify a sulphur content not exceeding 0.4 per cent., equivalent to some 245 grains per gallon. As this represents only about 0.01 per cent. by volume of sulphur dioxide in the exhaust gases it is apparent that neither a malodorous exhaust nor any appreciable corrosion need be feared. Moreover, sulphur dioxide can only cause corrosion when it is dissolved in water (in the liquid state) and its effects must, therefore, be limited to the cooler portions of the engine, *i.e.*, the silencer and possibly some parts of the exhaust pipe.

### Deposits

In the early days of benzol as a motor fuel "gumming" was frequently experienced, due to the deposition of resinous matter. In the process of rectification as now practised—drastic acid

washing followed by final distillation—the hydrocarbons which gave rise to these resins by polymerisation are almost entirely removed, partly in the acid tar and partly in the residue from the subsequent distillation. This trouble has, therefore, disappeared, but carbon deposits may be formed and these are in every case due to incomplete combustion. Such deposits always occur, of course, when petrol is used, and with suitable adjustment of the carburettor no more—and frequently less—carbon will be formed when running on benzol. In the Automobile Association run of 10,000 miles, for instance, the total deposit on the four pistons amounted to only  $6\frac{1}{2}$  grammes after the combustion of 406 gallons of benzol. Dr. Watson has stated that “so long as the mixture strength is properly adjusted, the carbon deposit is no worse than with petrol.”

### Lubrication

It has been thought that the use of benzol in motors might have an adverse effect on the lubricating oil and hence on the general mechanism of the system of lubrication. Benzol certainly appears to coagulate vegetable oils, but has now been proved to have no effect on the usual grades of mineral oils used. The high figures obtained for “miles per gallon of lubricating oil” in the A.A. long-distance tests are ample evidence of the immunity of benzol from this disadvantage. The lubricating systems of both the engines tested were carefully examined and in neither case was any adverse effect noticed; nor was any benzol found in the oil removed from the sump.

### Economical Consumption

The point which is of most importance to the average motorist is, perhaps, the relative economy in use of the two fuels. Benzol here has a decided advantage, as one would expect from a consideration of the relative calorific values, average figures for which are given in *Table 29*.

TABLE 29.—CALORIFIC VALUES OF MOTOR FUELS (*Brame*).

FUEL.	SPECIFIC GRAVITY.	CALORIFIC VALUE.	
		B.Th.U. per lb.	B.Th.U. per gallon.
Petrol (pre-war) .	0.680—0.760	18,450	132,500
Benzol (90's) .	0.883	17,100	150,000
Methylated alcohol .	0.820	10,350	84,900

The motorist thinks of fuel in terms of gallons—not of pounds—and from his point of view the calorific value of benzol is approxi-

mately 13 per cent. higher than that of petrol. When benzol is used in the engine not only is more power available, but the thermal efficiency of the engine is usually found to have increased. But the practical standard is mileage per gallon, and, given a suitable mixture, benzol is superior to petrol in this respect. The high mileage figures obtained in the A.A. & R.A.C. tests are evidence of this, and may be supplemented by a number of authoritative trials the results of which have been published during the past ten years. The average of seven such tests, made by different observers on different types of car, gives an increase in miles per gallon of 22.7 per cent. These tests were all taken without alteration to the compression ratio of the engine; but owing to the temperature of spontaneous ignition of benzol being higher than that of petrol, the compression, which is usually 70 or 75 lbs. per square inch in a petrol engine, may safely be increased to 150 lbs. in the case of benzol—with obvious further economy.

The rate of propagation of the flame when using benzol is less than that in a petrol-air mixture. There is, in consequence, a marked reduction of any tendency to "knock" under heavy loads, and the ignition may be advanced to a greater extent with a view to eliminating this knock and its serious effects on the engine.

### Alcohol as a Fuel

With a rapidly increasing demand for motor spirit it would appear that alcohol is the fuel of the future, as was foretold by the late Professor V. B. Lewes and others. In this connection the value of benzol is undoubted; for whilst alcohol possesses many advantages—chiefly in cheap production at home, and in the use of high compressions up to 200 lbs. per square inch—it also presents disadvantages. In the first place alcohol must be "denatured." Secondly, the volatility of alcohol is low, and for fuel purposes it requires the addition of a more volatile "livening agent." Alcohol will not mix freely with petrol, but alcohol and benzol are miscible in all proportions. It seems, therefore, probable that such a mixture will be the standard home-produced fuel of the not distant future, and there is little doubt the rapid development of road and air transport will absorb in this manner all the benzol we are able to produce at both coking plants and gasworks.

### Distribution of Motor Spirit

To render efficient service, a motor fuel, however satisfactory in other respects, must be made available to the motorist to at least the same extent as our present petrol supply. One of the early difficulties in the marketing of motor benzol was soon encountered in the impossibility of suitable distribution from a

large number of isolated producers. This was, however, soon overcome by the formation among those producers of the National Benzole Association. This organisation has done, and is doing, very valuable work both in distribution problems and in matters of standardisation, testing, etc. The Association now possesses large fleets of rail-tanks and motor lorries together with the requisite drums and cans. As the result of this enterprise the distribution of the spirit is controlled by the producers themselves, and a standard quality of motor benzol may be obtained at a very large number of garages and dépôts throughout the country. The gas engineer who contemplates the production of benzol need not, therefore, entertain any doubts as to the marketing of the spirit.

## CHAPTER XIX

### SUBSIDIARY USES FOR BENZOL PRODUCTS

It has been shown that the chief uses for benzol and its products are for motor fuel, and as the basis of the dyestuffs, explosives and synthetic chemical industries. There is, however, a large industrial demand for these bodies in many other directions, and their application depends, as a rule, upon the solvent properties and volatility of the spirits. Large quantities of benzol, toluol and solvent naphtha are used in the so-called "dry cleaning" process. The hydrocarbons are excellent solvents for grease, and the material is cleaned by the solution of any grease and by the consequent loosening and washing out of any insoluble dirt. Drying of the material is easily accomplished, without damage, owing to the volatile nature of the solvent. A somewhat similar use of these liquids is in the extraction of oils and fats, not only in the laboratory, but in many manufacturing operations. Apart from these uses, the application of benzene hydrocarbons in the rubber industry is probably the most important. Benzol products—particularly "solvent naphtha," a mixture containing principally xylenes—have a very high solvent power with regard to rubber, and the rubber solution of the cyclist is one of the commonest applications. The manufacture of such products as insulating materials, artificial leather, etc., entail the use of benzol and naphtha.

Many paints, stains, varnishes and lacquers contain benzol, and solvent naphtha is used in the mixing of printers' ink as a solvent for the greasy vehicle carrying the pigment. The various mixtures used as aeroplane "dope," with which the canvas coverings of the planes are made air- and water-tight, are benzol solutions, and very large quantities of benzol were used in this connection during the war.

In the past, when gas undertakings were penalised on an illuminating power standard, the majority used benzol (usually 90's benzol) for enrichment purposes, the spirit being vaporised into the gas. This demand has now ceased, and the application is only of interest in the case of local enrichment where a large number of flat flame burners are in use through force of exceptional circumstances. Lighting, however, still claims a fair proportion of the naphtha made, in the form of burning naphtha for lamps—a product which gives about 80 per cent. below 200° C. Solvent naphtha readily dissolves naphthalene and forms an



excellent "carrier," and although kerosene is to be preferred for this purpose, many engineers vaporise or atomise solvent naphtha into the gas leaving the holders.

Forerunnings, or "fronts," represent some 2—3 per cent. of the crude benzol, and the mixture usually drops at about  $40^{\circ}\text{C}$ ., giving some 85 or 90 per cent. below  $80^{\circ}\text{C}$ . It has been suggested that this should be returned to the gas, but such a policy is open to serious objection on account of its high content of carbon bisulphide. Once the sulphur is extracted from the gas it should not be put back; and whilst forerunnings are sometimes difficult to dispose of, the best practice seems to be to allow them to accumulate and then redistil with a view to recovering as much of the contained benzene as possible. It is difficult, however, to approach complete separation—otherwise there would be no forerunnings—and it is commercially impracticable to extract the carbon bisulphide in a usable form. Where, however, the latter compound is extracted by a process such as that of Adam or Wilson (p. 138), a cheap source of carbon disulphide presents itself, and this should find ready application in the viscose process of artificial silk manufacture. Viscose is the trade name for cellulose sodium xanthate, the starting point of the process.

The applications of naphthalene, in addition to its use as a basis of dyes and explosives, are many. The crude substance taken from the settling pans, and pressed or "whizzed," forms an excellent fire-lighter, and for this purpose is incorporated with wood shavings or chips. The purified hydrocarbon finds use as "moth-balls" or in stick form as the disinfectant known as "carbon." It may also be utilised as a fuel with good results, owing to its high calorific power and vapour tension, and forms a constituent of many patented motor spirits. Willis and Wilson (*Gas World*, Dec. 15th, 1917, p. 445) have described a carburettor by means of which they successfully ran a motor boat on naphthalene alone, and this fuel has been used for locomotives on some of the French railways. In this case the air entering the cylinders is passed over molten naphthalene contained in a steam-jacketed reservoir, the motor being started on petrol by means of an auxiliary carburettor.

The residues resulting from the various stages of benzol production are relatively small and of little consequence. Reference has already been made to the disposal of the acid tar resulting from the acid washing of the crude spirit. This residue is boiled with steam, and the resulting pitchy solid may either be burnt or carted to the tip.

Residues from the various distillations of the crude benzol are commonly returned, after separation of the naphthalene, to the wash-oil. Spent wash-oil is best disposed of to the tar distiller, the absence of naphthalene and tar acids making it of little use for such purposes as the "pickling" of timber.

In conclusion we may note two patented processes. The first,

due to Koppers (*Brit. pat.*, 112419), aims at the production of useful resins from benzol-still residues, by dissolving them in a suitable solvent and subsequent distillation. In the second process J. T. Sheard (*Brit. pat.* 9636) treats certain troublesome effluents from a rectification plant with alum. The precipitate formed is allowed to settle, and from it are obtained "valuable hydrocarbons and a residue suitable for use as a lubricating oil." These processes are only of interest in the case of very large installations.

# APPENDIX A

## ANALYSIS OF CRUDE BENZOL BY DR. COLMAN'S METHOD

IN this Appendix an abstract is given of the methods described by Colman and Yeoman (*Jour. Soc. Chem. Ind.*, 1910, **38**, 57, T.) so far as these relate to the analysis of crude benzol. In carrying out the analysis of these products, correct results can only be obtained by strict adherence to the conditions of distillation set down, which owing to lack of space cannot be repeated here, and for which reference must be made to the original paper.

A known volume of the sample (250—500 c.c.) is directly fractionated from a round-bottomed flask, fitted with a Young's 12-bulb pear column, at the rate of 4 c.c. per minute, and the fraction up to 200° C. collected. The quantity of the original sample taken should be such as will give at least 200 c.c. at this temperature.

This fraction is shaken with one quarter of its volume of 10 per cent. aqueous caustic soda, allowed to settle, the caustic layer run off, and the oil washed with water. This is also run off and the volume of the residual oil measured. The loss of volume represents approximately the volume of tar acids in the quantity of oil taken. The remaining oil is then shaken for five minutes with 8 per cent. of its volume of concentrated sulphuric acid (95 per cent. strength) and allowed to settle for fifteen minutes. Water is then carefully added down the side of the separating funnel, the acid layer run off, and the oil washed by allowing a thin stream of water to fall through it without shaking. The oil is then shaken gently with 10 per cent. aqueous caustic soda and finally again with water. The further reduction in volume gives approximately the volume of unsaturated hydrocarbons (chiefly olefines) which have been absorbed by the sulphuric acid.

The purified oil, after freeing from water as completely as possible, is again distilled with column, as before, and the following fractions collected :—

(a) Up to 90° C., containing only benzene and toluene together with carbon bisulphide, and paraffins of similar boiling point.

(b) 90°—140° C., consisting of benzene, toluene and xylene except for paraffins of similar boiling point.

(c) 140°—160° C., consisting of xylenes, cumenes, etc., with paraffins.

(d) 160°—200° C., containing higher homologues of benzene, with some paraffins.

(e) Residue at 200° C., consisting chiefly of the polymerised hydrocarbons formed by the action of sulphuric acid on the dienes, etc., in the original sample.

### Analysis of the Fractions

The percentage composition of fractions (a) and (b) are determined by distillation under specified conditions, the volumes of the fractions obtained being compared with corresponding fractions resulting from a similar distillation of mixtures of the pure hydrocarbons. The apparatus required consists of:—

(i.) A standard Engler 100 c.c. distillation flask having the following dimensions:—Internal diameter of bulb, 6.5 cm.; length of neck, 15.0 cm.; internal diameter of neck, 1.6 cm.; vertical height of side tube above level of liquid when flask is charged with 100 c.c., 9.0 cm.; angle of side tube, 75 degrees. Flasks which do not vary by more than 3 per cent. from any of these dimensions may be employed.

(ii.) An efficient water-cooled condenser, preferably a 10-inch Liebig condenser placed vertically.

(iii.) A set of calibrated glass cylinders (50 and 100 c.c.).

(iv.) An accurate thermometer, graduated in  $\frac{1}{5}^{\circ}\text{C}$ . from  $70^{\circ}$ — $130^{\circ}$ , and placed with the top of the bulb just below the bottom of the side tube of the Engler flask. Great care must be exercised in employing an accurately calibrated thermometer, and the readings must be corrected for barometer in the manner specified in the original paper.

The distillation is performed by introducing a measured quantity of the fraction under test into the Engler flask and distilling the same at a rate of 7 c.c. per minute, the flame of the burner being extinguished at each point of interruption.

#### *Fraction Up to $90^{\circ}\text{C}$ ., and Commercial Benzol*

One hundred cubic centimetres of the sample (or less if the available quantity is insufficient) are distilled in this manner up to a temperature of either  $85^{\circ}\text{C}$ . (corrected) or  $90^{\circ}\text{C}$ . (corrected). The percentage of toluene is read off from the Benzene-Toluene Graph (FIG. 64), the percentage of benzene being found by difference.

It must be noted that these percentages of benzene and toluene include any carbon bisulphide or paraffins which may be present. These may be separately estimated from the specific gravity of the fractions before and after extraction with alcoholic caustic soda, by means of a graph given in the original paper.

In analysing samples of commercial benzol by this method it may be necessary to modify slightly the distillation in order to apply the graph. Thus if the percentage of toluene is below 3—4 per cent., a mixture of 95 c.c. of the sample with 5 c.c. of pure toluene is distilled to  $85^{\circ}\text{C}$ . (corrected) and this 5 c.c. of toluene deducted from the percentage found.

#### *Fraction $90^{\circ}$ — $140^{\circ}\text{C}$ . and Commercial Toluol.*

One hundred cubic centimetres of this fraction are distilled from the Engler flask in exactly the same manner as in the preceding case, and the volumes of the following fractions (which should total to at least 99.5 c.c.) are noted: up to  $105^{\circ}\text{C}$ . (corrected),  $105^{\circ}$ — $116^{\circ}\text{C}$ . (corrected), and above  $116^{\circ}\text{C}$ . The percentages of benzene and toluene are read off directly from the Benzene-Toluene-Nylene Graph (FIG. 65), the percentage of xylene being found by difference.

Should the volume of either fraction be insufficient to give a reading on the graph, the distillation is repeated after adding known proportions of pure benzene or pure xylene as the case may be. Carbon











disulphide is rarely present in appreciable quantities in this fraction ; paraffins must be again corrected for by the specific gravity method, using a graph accompanying the paper from which this abstract is taken.

*Fraction 140°—160° C. and Commercial Solvent Naphtha*

If to the percentage of this fraction found there is added the percentage of xylene found in the fraction 90°—140° C., the combined figure gives an approximate estimation of the quantity of commercial solvent naphtha contained in the original sample.

Each 0.001 that the specific gravity of a sample of xylene or solvent naphtha is below 0.868 indicates the presence of approximately 1 per cent. of paraffins.

*Fraction 160°—200° C.*

The amount of this fraction indicates approximately the amount of " heavy solvent naphtha " contained in the original sample.

# APPENDIX B

## USEFUL DATA AND TABLES

### USEFUL DATA.

1 cubic foot of water = 62.4 lbs. = 6.24 gallons.  
 1 cubic foot of air at 0° C. and 760 mm. = 0.0807 lb.  
 1 cubic foot of hydrogen at 0° C. and 760 mm. = 0.00557 lb.  
 Volume of 1 gramme-molecule of any vapour = 22.4 litres.  
 Volume of 1 ounce-molecule of any vapour = (very nearly) 22.4 cubic feet.  
 1 atmosphere = 14.7 lbs. per square inch = 2,116.8 lbs. per square foot = 760 mm. of mercury.  
 1 lb. per square inch = pressure of a column of water 2.3 feet high.  
 $\pi = 3.1416$ .  $\pi^2 = 9.87$ .  
 1 horse-power = 33,000 foot-lbs. per minute = 746 watts.  
 Grammes per 10 c.c. = lbs. per gallon.  
 1 gallon per minute = 9.62 cubic feet per hour.

### METRIC EQUIVALENTS.

WEIGHT.	LENGTH.	VOLUME.
1 gm. = 15.43 grs. 1 kg. = 2.205 lbs.	1 cm. = 0.394 in. 1 metre = 39.37 in. = 3.28 ft.	1 c.c. = 0.061 c. in. 1 litre = 0.0353 c. ft. = 0.22 gallon. = 1.76 pints.
1 oz. = 28.35 gm. 1 lb. = 453.6 gm. 1 cwt. = 50.8 kg.	1 in. = 2.54 cm. 1 ft. = 30.48 cm. 1 yd. = 0.914 metre.	1 c. in. = 16.39 c.c. 1 c. ft. = 28.315 l. 1 gallon = 4.54 l. 1 pint = 568 c.c.

### SPECIFIC GRAVITY.

To convert degrees Twaddell into Specific Gravity, multiply by 0.005 and add 1.

#### STRENGTH AND SPECIFIC GRAVITY AT 15° C. OF SOLUTIONS OF SODIUM HYDROXIDE (*Bayley*).

Percentage NaOH.	Specific gravity.	Percentage NaOH.	Specific Gravity.
5	1.059	40	1.437
10	1.115	45	1.488
15	1.170	50	1.540
20	1.225	55	1.591
25	1.279	60	1.643
30	1.332	65	1.695
35	1.384	70	1.748

STRENGTH AND SPECIFIC GRAVITY AT 15° C. OF SOLUTIONS OF  
SULPHURIC ACID (*Lunge and Isler*).

Specific gravity.	° Tw.	Percentage H <sub>2</sub> SO <sub>4</sub> .	Specific gravity.	° Tw.	Percentage H <sub>2</sub> SO <sub>4</sub> .
1.505	100	59.70	1.725	145	79.36
1.525	105	60.06	1.750	150	81.56
1.550	110	64.26	1.775	155	83.90
1.575	115	66.30	1.800	160	86.90
1.600	120	68.51	1.820	164	90.05
1.625	125	70.74	1.825	165	91.00
1.650	130	72.82	1.830	166	92.10
1.675	135	74.97	1.836	167	93.43
1.700	140	77.17	1.840	168	95.60

## NUMBER OF GALLONS IN 1 TON OF LIQUIDS OF DIFFERENT SPECIFIC GRAVITIES.

*To nearest 0.1 gallon.*

Specific gravity.	Gallons per ton.	Specific gravity.	Gallons per ton.	Specific gravity.	Gallons per ton.
0.850	263.5	0.920	243.5	0.990	226.3
0.860	260.5	0.930	240.9	1.000	224.0
0.870	257.5	0.940	238.3	1.010	221.8
0.880	254.5	0.950	235.8	1.020	219.6
0.890	251.7	0.960	233.3	1.030	217.5
0.900	248.9	0.970	230.9	1.040	215.4
0.910	246.2	0.980	228.6	1.050	213.3

## METALS USED IN BENZOL PLANT CONSTRUCTION.

METAL.	Specific gravity.	Weight of 1 cubic inch. Lbs.	Weight of 1 square foot, ¾ inch thick. Lbs.	COEFFICIENT OF EXPANSION.		Specific heat.	Relative heat conductivity.
				Per 1° C.	Per 1° F.		
Mild steel .	7.8	0.282	20.3	.0000110	.0000061	0.1158	1.30
Wrought iron	7.85	0.284	20.4	.0000119	.0000066	0.1146	1.74
Cast iron .	7.4	0.268	19.6	.0000102	.0000057	0.1250	1.57
Lead .	11.4	0.412	29.6	.0000280	.0000155	0.0314	1.00

## TEMPERATURE CONVERSION.

$$^{\circ}\text{C.} = (^{\circ}\text{F.} - 32) \times \frac{5}{9}$$

$$^{\circ}\text{F.} = \left(^{\circ}\text{C.} \times \frac{9}{5}\right) + 32.$$

## CORRECTION OF THERMOMETER READINGS.

(See approximate method, p. 129.)

(a) For barometer :—

$$\text{Correction} = 0.00012 (760 - p) (273 + t^{\circ})^{*}.$$

Where  $p$  = height of barometer in millimetres (corrected to  $^{\circ}\text{C.}$ ).

$t^{\circ}$  = the boiling point to be corrected.

\* Within the range  $80^{\circ}$ — $120^{\circ}\text{C.}$  the following table may be used in place of formula (a) for ascertaining the barometric correction (Colman) :—

$p$ .	Corr.	$p$ .	Corr.	$p$ .	Corr.
772	— 0.55	754	+ 0.30	736	+ 1.10
770	— 0.45	752	+ 0.35	734	+ 1.15
768	— 0.35	750	+ 0.45	732	+ 1.25
766	— 0.30	748	+ 0.55	730	+ 1.35
764	— 0.20	746	+ 0.65	728	+ 1.45
762	— 0.10	744	+ 0.75	726	+ 1.50
760	Nil.	742	+ 0.85	724	+ 1.60
758	+ 0.10	740	+ 0.90	722	+ 1.70
756	+ 0.20	738	+ 1.00	720	+ 1.80

(b) For Stem Immersion :—

$$\text{Correction} = 0.000143 (T - t)N.$$

Where  $T$  = observed boiling point.

$t$  = temperature of air around unheated stem.

$N$  = length of exposed mercury column in scale degrees.

## CONVERSION OF THERMAL UNITS

B.Th.U.	Large calorie.	Small calorie.	Lb.-cent. unit. C.H.U.	Foot-pound.
1	0.252	252	0.555	778
3.9682	1	1,000	2.2046	3,080
0.003968	0.001	1	0.002046	3.08
1.8	0.4536	453.6	1	1,397

## SPECIFIC HEATS.

## LIQUIDS.

Water	.	.	.	.	1.00
Benzene	.	.	.	.	0.34
Toluene	.	.	.	.	0.40
Creosote, about	.	.	.	.	0.4

## GASES AND VAPOURS (at constant pressure).

Oxygen	.	.	.	.	0.242
Nitrogen	.	.	.	.	0.235
Air	.	.	.	.	0.237
Carbon dioxide	.	.	.	.	0.202
Water vapour	.	.	.	.	0.465
Benzene	.	.	.	.	0.299
Carbon disulphide	.	.	.	.	0.160
Ammonia	.	.	.	.	0.520

## LAGGING.

One hundredweight of asbestos boiler-covering composition (weighed dry) covers about 16 square feet to a thickness of 2 inches.

## PROPERTIES OF SATURATED STEAM

ABSOLUTE PRESSURE. Lbs. per square inch.	TEMPERATURE.		VOLUME. Cubic feet per lb.	LATENT HEAT.	SENSIBLE HEAT.
	° C.	° F.		B.Th.U. per lb.	
14.7	100	212	26.5	965.8	180.8
20	108.3	227	19.9	954.8	196.7
30	121.0	250	13.6	939.0	219.3
40	130.5	267	10.4	927.0	236.4
50	138.3	281	8.41	917.3	250.4
60	144.6	292	7.03	908.9	262.2
65	147.5	298	6.50	904.1	268.7
70	150.2	303	6.11	901.6	272.7
75	152.8	307	5.70	897.3	278.4
80	155.4	312	5.40	895.1	281.9
85	158.5	316	5.10	891.1	287.2
90	160	320	4.84	889.2	290.4
95	162.2	324	4.60	885.3	295.5
100	164	327	4.39	883.8	298.1
105	166	331	4.19	881.2	301.7
110	168	334	4.01	878.7	305.2
115	170	338	3.85	876.4	308.6
120	171.7	341	3.70	874.1	311.9
130	175	347	3.44	869.7	318.1
140	178.2	353	3.20	865.5	324.0
150	181.2	358	3.01	861.6	329.6
160	184	363	2.84	857.9	334.8

### VAPOUR TENSION OF WATER

(For Vapour Pressure of other Liquids, see FIG. 2, p. 19.)

Temperature. ° C.	Vapour tension. Millimetres mercury.	Temperature. ° C.	Vapour tension. Millimetres mercury.
0	4.6	40	55.1
5	6.5	50	92.3
10	9.2	60	149.2
15	12.8	70	233.5
20	17.5	80	355.1
25	23.7	90	525.8
30	31.7	100	760.0
35	42.0		

### CORRECTION OF GAS VOLUMES

$$V = v \times \frac{17.64 (h - a)}{460 + t}$$

Where  $V$  = volume at 60° F. and 30 inches (moist).

$v$  = volume of gas measured (moist).

$h$  = height of barometer in inches.

$a$  = tension of aqueous vapour (in inches mercury) at  $t^\circ$ .

$t$  = temperature, ° F.

### CALIBRATION OF CYLINDRICAL TANKS

Area of a circular segment :—

$$A = \frac{4}{3} X \sqrt{(0.625 X)^2 + C^2}$$

Where  $X$  = height of segment.

$C$  = the semi-chord.

For ascertaining the contents of a flat-ended cylindrical tank, the following table may be used. If  $D$  = the "dip" of the tank expressed as a percentage of the diameter, the corresponding value of  $V$  = the volume of liquid in the tank expressed as a percentage of its total volume.

$D$ per cent.	$V$ per cent.	$D$ per cent.	$V$ per cent.	$D$ per cent.	$V$ per cent.
0.5	0.06	32.5	28.17	70.0	74.78
1.0	0.17	35.0	31.18	72.5	77.70
1.5	0.31	37.5	34.24	75.0	80.46
2.5	0.67	40.0	37.35	77.5	83.17
5.0	1.87	42.5	40.49	80.0	85.77
7.5	3.41	45.0	43.66	82.5	88.25
10.0	5.20	47.5	46.85	85.0	90.60
12.5	7.21	50.0	50.00	87.5	92.79
15.0	9.40	52.5	53.15	90.0	94.80
17.5	11.75	55.0	56.34	92.5	96.59
20.0	14.23	57.5	59.51	95.0	98.13
22.5	16.83	60.0	62.65	97.5	99.33
25.0	19.54	62.5	65.76	98.5	99.69
27.5	22.30	65.0	68.82	99.0	99.83
30.0	25.22	67.5	71.83	99.5	99.94

The best method of using above table is to plot a curve (of gallons against inches) for each individual tank. From this the contents at any "dip" may be read off.

## CONSTITUENTS OF CRUDE BENZOL

*(Spielmann and others.)*

CONSTITUENT.	FORMULA.	Molecular weight.	Specific gravity at 15° C.	Melting point. ° C.	Boiling point. ° C.
Benzene	$C_6H_6$	78	0.885	5.5	80.3
Toluene	$C_6H_5.CH_3$	92	0.870	-90	110.8
Ortho-xylene	$C_6H_4(CH_3)_2$	106	0.868	-28	142-143
Meta-xylene.	$C_6H_4(CH_3)_2$	106	0.869	-55	139
Para-xylene.	$C_6H_4(CH_3)_2$	106	0.866	15	138.5
Cumene	$C_9H_{12}$	120	0.850	—	153
Naphthalene.	$C_{10}H_8$	128	1.15 (a) 0.977 (b)	79.6	218
Carbon disulphide	$CS_2$	76	1.272	-108	46.2
Thiophene	$C_4H_4S$	84	1.070	—	84.1
Thiotolene	$C_5H_6S$	98	1.019	—	112
Phenol.	$C_6H_5.OH$	94	1.065	42.2	184
Ortho-cresol	$C_6H_4.CH_3.OH$	108	—	31	188
Meta-cresol	$C_6H_4.CH_3.OH$	108	—	5	201
Para-cresol	$C_6H_4.CH_3.OH$	108	—	36	198
Pyridine	$C_5H_5N$	91	0.978	-42	115
Hexane	$C_6H_{14}$	86	—	—	69
Heptane	$C_7H_{16}$	100	—	—	98
Octane.	$C_8H_{18}$	114	—	—	125.5

(a) Solid, cast, at 15° C.

(b) Liquid at 80° C.





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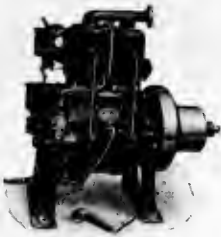
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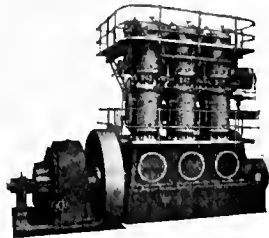


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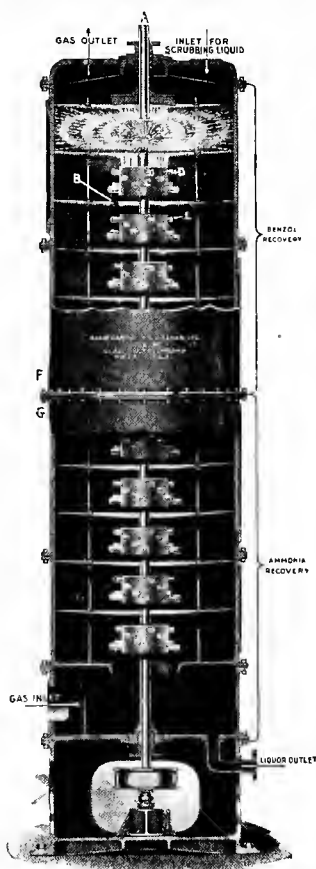
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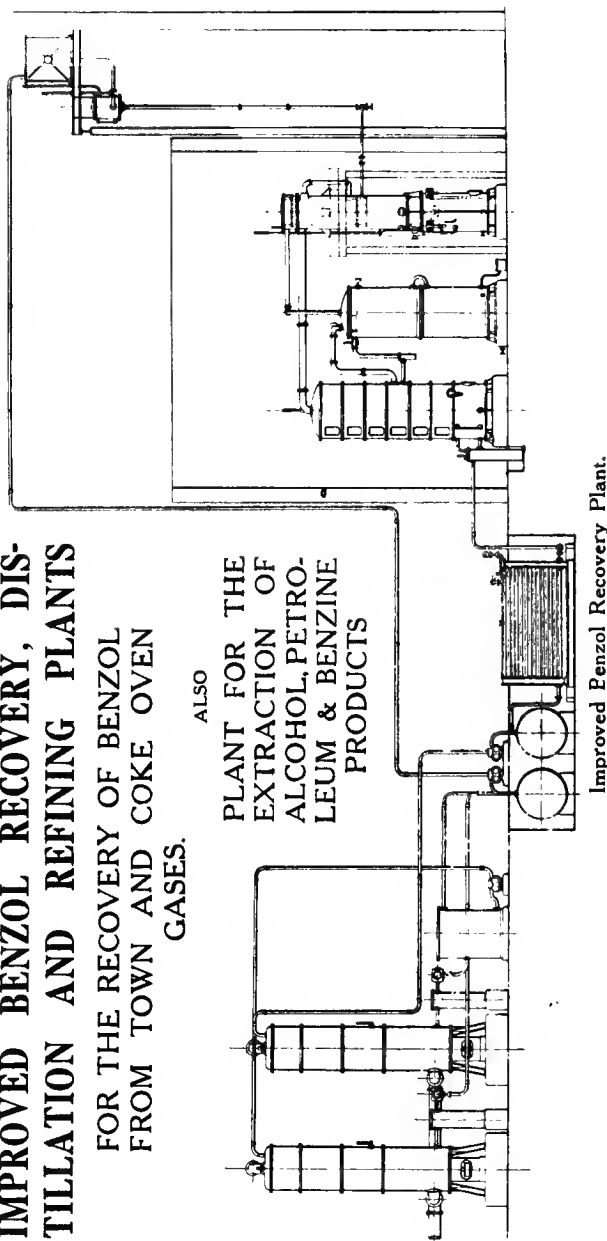
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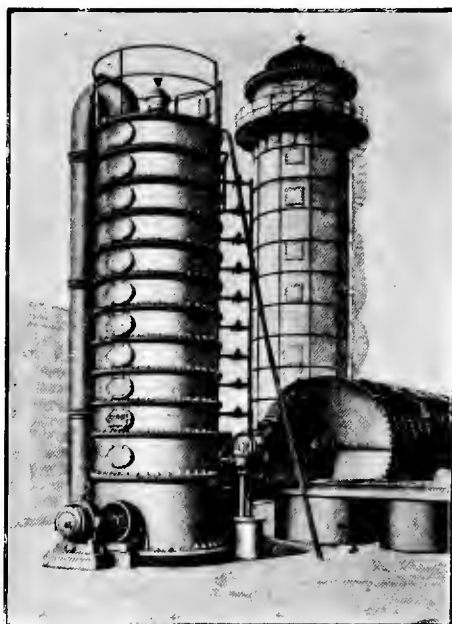
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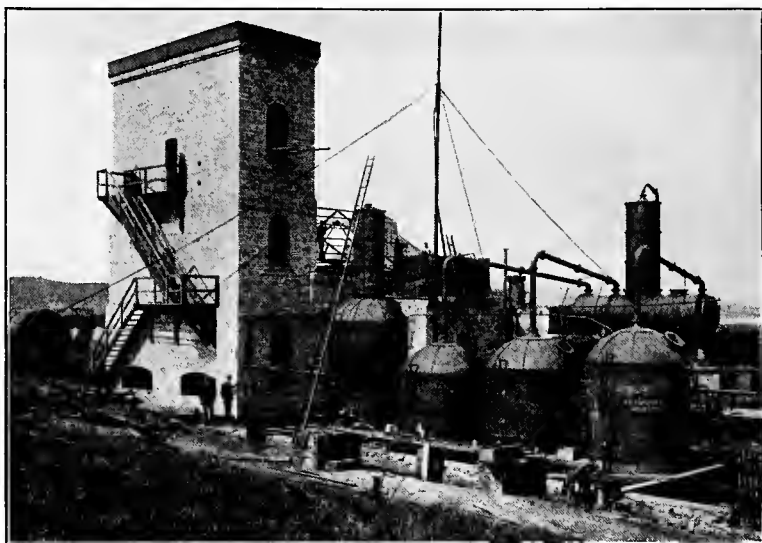
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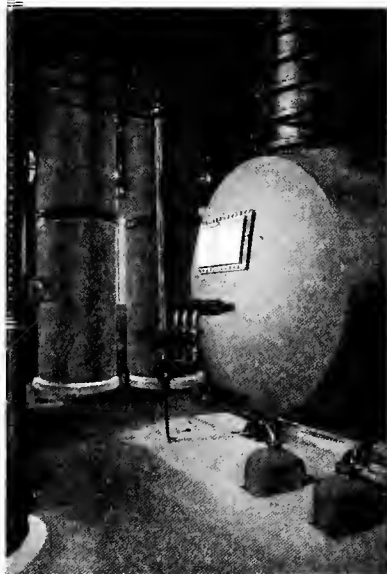


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